The Impact of Green Infrastructure on Stormwater Quality:
A Sewershed-Scale Analysis of the Effects of Blueprint Columbus on Nutrients, Sediments, and Metals

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Abstract:

The discharge of pollutants to surface waters via stormwater runoff is a societal challenge. Among other impacts, these pollutants cause harmful algal blooms and eutrophication resulting in degraded water quality, threats to public health and potable water, and reduced tourism, cultural activities, and coastal economies. Waterborne

pollutants can be unsightly, including plastics, garbage, and sediment, or less visible, including nutrients and soluble metals. Stormwater runoff is a major source of nutrients, sediment, and metals to aquatic ecosystems. Green infrastructure (GI) is a novel way to reduce stormwater to improve water quality to protect ecosystems, public health, and coastal economies. While the ability for GI to reduce stormwater pollution has been demonstrated for single installations and at a smaller scale of less than 10 ha, there are still important unknowns about water quality benefits of a network of GI across entire sewersheds. These questions were the focus of this research.

GI reduces directly connected impervious area through the use of stormwater control measures including bioretention cells and permeable pavement. Using soil and plants as natural filters, these solutions have been shown to individually improve water quality. This improvement is made possible by increasing sewershed storage and infiltration to counter impermeable surfaces typical in urban areas. As part of the Blueprint Columbus project, several hundred bioretention cells and 8,742 m^2 of permeable pavement roads have been implemented in the Clintonville neighborhood of Columbus, OH. Also, redirecting downspouts, implementing sump pumps, and lining sanitary sewer laterals have been used to lessen sanitary sewer overflows, and large underground tunneled to lessen combines sewer overflows. Bioretention and permeable pavement are the focus of this thesis.

Using automated samplers, event mean water quality samples were collected and analyzed for nutrients, sediment, and metals over three and a half years at the outfall of three sewersheds (11.5 to 111.5 ha) located in the Clintonville neighborhood of Columbus, Ohio. Tipping bucket rain gauges and flow meters were utilized to characterize sewershed hydrology. GI was installed in two sewersheds while the third served as a control to account for annual and seasonal changes in rainfall, runoff, and pollutant generation. A before-after, control-impact paired sewershed approach was applied to obtain a robust comparison of pollutant concentrations and loads before and after the installation of GI.

Water quality samples were collected at the discharge point of three sewersheds located in the Clintonville neighborhood of Columbus, Ohio. A network of various technologies, including tipping rain gauges, area-velocity meters, and ISCO water samplers were utilized to continuously collect water quality data, including nutrients, sediment, and metals. This network was able to sense precipitation and collect samples throughout the duration of the precipitation event, producing event mean pollutant concentrations. Pollutant loads were calculated as the product of this event mean pollutant concentration and measured stormwater runoff volume.

Total nitrogen, phosphorus, and suspended solid concentrations decreased by 13.7-24.1, 20.9-47.4, and 61.6-67.7%, respectively. Loads reductions for these pollutants were in the range of 24.0-25.4, 27.8-32.6, and 59.5-78.3%, respectively. Significant reduction in both particulate and dissolved pollutants were observed due to GI installation at a sewershed scale. Lead, copper, and zinc concentrations decreased in the range of 25.2-58.3% and loads in the range of 21.3-52.3%. Storm event loads were significantly reduced for every

heavy metal analyzed herein. Bioretention was better suited to treat TSS, Cu, and Pb for smaller storm events. Since these results are for 1 or 2 years following the installation of GI, inherent limitations exist with sampling size, especially when trying to make statistical conclusions with 1 year of post-GI data. Sustained monitoring will be needed to evaluate future impacts of the system on water quality.

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Chapter 1. Quantifying the Effects of Green Infrastructure on Nutrients and Sediment in Stormwater: A Sewershed-scale Analysis

1.0 Abstract

Urban stormwater runoff is a substantial source of nutrients and sediment to aquatic ecosystems. Green infrastructure (GI), including bioretention and permeable pavement, is a novel way to treat stormwater pollutants to improve water quality. Using soil and plants as natural filters, these solutions have been shown to improve water quality at the site scale, but little evidence exists regarding their performance at a neighborhood-scale. The Blueprint Columbus project is an effort by the city of Columbus, Ohio, to retrofit green infrastructure (among other solutions) to eliminate sanitary sewer overflows in the city. The research herein is focused on the combined effects of many GI systems on water quality at a sewershed scale. We quantified water quality changes at 11.5 and 47.8 ha sewersheds as a result of GI implementation using a before-after, control-impact (BACI) paired-watershed approach. Water quality samples using automated samplers were collected over three and a half years at the outfall of one control and two treatment sewersheds located in the Clintonville neighborhood of Columbus, Ohio. A network of rain gauges and flow meters were used in support of pollutant load determination. Significant reductions in nutrients, both particulate and dissolved, and sediment were observed with the adoption of GI. Total nitrogen, phosphorus, and suspended solid concentrations decreased by 13.7-24.1, 20.9-47.4, and 61.6-67.7%, respectively. Loads

reductions for these pollutants were in the range of 24.0-25.4, 27.8-32.6, and 59.5-78.3%, respectively. GI was better suited to treat TSS for smaller storm event, and nitrogen and phosphorus pollutant removals were similar regardless of storm size. Having fewer GI practices, yet treating a larger percent of the sewershed resulted in greater particulate removal. These results demonstrate during the first years of implementation, GI is effective in reducing event mean concentrations and storm event loads.

1.1 Introduction

Urbanization results in the construction of impermeable surfaces, leading to higher volumes of impaired runoff (Goonetilleke et al., 2005), which negatively affect biodiversity and ecosystem functions (Wu et al., 2011), public health (Hathaway et al., 2015; Lim et al., 2015), the economy (Hellman et al., 2018), and ecosystem services (Marsalek & Rochfort, 2004; Stepenuck et al., 2002). Stormwater runoff in urban areas is a substantial conveyance for anthropogenic and natural pollutants, both dissolved and particulate, to enter waterways. Fertilizers, vehicle emissions, and human and animal waste are sources of dissolved nutrients, namely nitrogen- and phosphorus, in urban areas (Brinkmann, 1985; Yang & Toor, 2018). Construction sites, roads, and erosion are sources of sediment (i.e., particulates) into aquatic ecosystems (Ellis et al., 1987). Nutrients and sediment from urban stormwater runoff fuel eutrophication, resulting in rapid algal growth and hypoxia (Browman et al., 1979; Silva et al., 2019).

Low impact development (LID; Ahiablame et al., 2012; Dietz, 2007) is a land development strategy that mitigates negative impacts of urbanization by employing stormwater control measures (SCM). A subset of these include green infrastructure (GI) technologies, which passively improve stormwater quality and reduce stormwater runoff through infiltration and evapotranspiration (Chen et al., 2019). Bioretention cells, perhaps the most commonly used GI SCM, are designed with a sandy soil media and mimic natural runoff hydrology while treating stormwater runoff (DeBusk et al., 2011; Hsieh & Davis, 2005; Wang et al., 2017). These natural processes allow for sedimentation, filtration, microbially-mediated degradation, and sorption processes to occur, sequestering or breaking down nitrogen and phosphorus, heavy metals, and total suspended solids (Davis et al., 2006; Osman et al., 2019; Trowsdale & Simcock, 2011). Nitrogen removal in bioretention cells occurs through sedimentation of organic, particulate-bound nitrogen (Lusk et al., 2020), denitrification in the anoxic, internal water storage zone (if empoyed; Collins et al., 2010; Kim et al., 2003; Lopez-Ponnada et al., 2020) and through vegetative uptake (Muerdter et al., 2019; Shrestha et al., 2018). Nitrification also occurs in bioretention cells, where aerobic soil media permits the conversion of ammonia to nitrate (Fan et al., 2019). Bioretention cells reduce particulate phosphorus by sedimentation and filtration, and dissolved phosphorus through either vegetative uptake or binding to soil particle surfaces through sorption processes, especially to iron and aluminum oxides of clays and silt (Hunt et al., 2012; Lijklema, 1980; Muerdter et al., 2019; Song & Song, 2019). Total suspended solids (TSS) in urban stormwater runoff are removed by bioretention through filtration and sedimentation (Trowsdale & Simcock, 2011). Bioretention effectively mitigates pollutant loading by not only reducing pollutant concentrations, but also attenuating stormwater runoff volumes (Davis et al., 2009; Winston et al., 2016).

Permeable pavement, another form of GI consisting of a porous surface underlain by layers of open-graded aggregate, also treats stormwater and lessens the impacts of urban development (Brattebo & Booth, 2003). Unlike traditional pavement, permeable pavement allows for runoff volume reduction, groundwater recharge, and water quality improvement (Braswell et al., 2018; Roseen et al., 2012; Scholz & Grabowiecki, 2007; Winston et al., 2018). Through filtration and sedimentation, permeable pavement reduces organic and inorganic particulates in stormwater runoff (Kamali et al., 2017). Along with excellent particulate removal (i.e. the reason that it clogs), nitrification has been demonstrated in the aerobic voids and denitrification in the internal water storage zone (IWS), when applied (Bean et al., 2007; Braswell et al., 2018; C. Brown et al., 2009; Winston et al. 2016). Particulate phosphorus removal through sedimentation, and organic phosphorus removal through adsorption to soil underlying the aggregate and transformations by microorganisms have been observed within permeable pavement (Sansalone et al., 2008; Tota-Maharaj & Scholz, 2010).

Sanitary sewer overflows (SSO), which result from infiltration and inflow of stormwater runoff overwhelming the sanitary sewer capacity, are a source of degraded water quality in urban areas (Field & O'Connor, 1997). Cities across the country have used GI as part of their plans for SSO control. Columbus, Ohio has retrofitted hundreds of GI practices into a single neighborhood along with updating other stormwater infrastructure (i.e., redirecting downspouts, implementing sump pumps, and lining sanitary sewer laterals) as part of the Blueprint Columbus project. The goal of this work is to reduce SSOs (Pawlowski et al., 2014). This thesis chapter reports on an effort to quantify changes in stormwater quality after GI and stormwater infrastructure improvements were implemented across two sewersheds. For the purposes of the experiment herein, only the green infrastructure had been installed; the other infrastructure updated had not yet been or was in the process of being constructed.

While past studies have noted water quality improvements from GI at the site scale, no studies have evaluated impacts of more than a 10 ha sewershed. A 0.53 ha, residential catchment with sandy underlying soils in North Carolina experienced 58, 38, and 82% reductions in total nitrogen (TN), total phosphorus (TP), and TSS concentrations, respectively, with the adoption of an in-street bioretention cell, four permeable pavement parking stalls, and a tree filter treating 91% of the total sewershed drainage area (Page et al., 2015). Pollutant loads for TN, TP, and TSS decreased by 79, 72, and 91%, respectively. A 7.1 ha low impact development (LID) commercial site with eight bioretention cells, pervious concrete, and a constructed stormwater wetland in North Carolina demonstrated 16, 29, and 99% load removal for TN, TP, and TSS, respectively (Line et al., 2012). A 2.53 ha LID commercial site also in North Carolina treated by underground grey and aboveground GI, including grassed bioswales and bioretention, produced pollutant loadings <5% of those at a nearby conventional site (Wilson et al., 2015). However, a 1.7 ha LID residential sewershed in Connecticut with permeable pavers and twelve bioretention cells demonstrated a nitrogen pollutant export reduction, while TSS and TP exports increased due to stormwater flow through and fertilization of grass swales (Bedan & Clausen, 2009). While these previous studies have measured how GI impacts water quality, understanding how the density and size of GI retrofits affects water quality in adjacent sewersheds is a substantial gap in knowledge. Quantifying the levels of retrofitting needed in older neighborhoods without stormwater controls will provide guidance to municipalities adopting these practices at greater spatial scales.

The research objectives of this study address these knowledge gaps by 1) using a paired watershed approach to quantify changes in nutrients and sediment resulting from the implementation of GI on a sewershed scale, 2) discussing fundamental processes responsible for these water quality changes, 3) evaluating if GI is better suited for water quality treatment for smaller or larger storm events, and 4) comparing annual pollutant load reductions in two adjacent sewersheds with varying GI density.

1.2 Materials and Methods

1.2.1 Site Description

Three sewersheds in the Clintonville neighborhood of Columbus, Ohio were monitored for stormwater flow and water quality at their respective outfalls (Figure 1). The sewersheds were 3.6-17.4% commercial and institutional land use. The study region is single-lot, residential family plots constructed between 1910 and 1950. Soils in the neighborhood were mapped as silt loam in the Cardington and Bennington soil series (Table 1; NRCS Web Soil Survey, 2019). This region experiences four distinct seasons, with winter temperatures in the range of -6 to 3°C, and summer temperatures in the range of 18 to 29°C. Long-term average annual precipitation is 1,000 mm, including an average of 70 mm of snowfall (NOAA 2020).

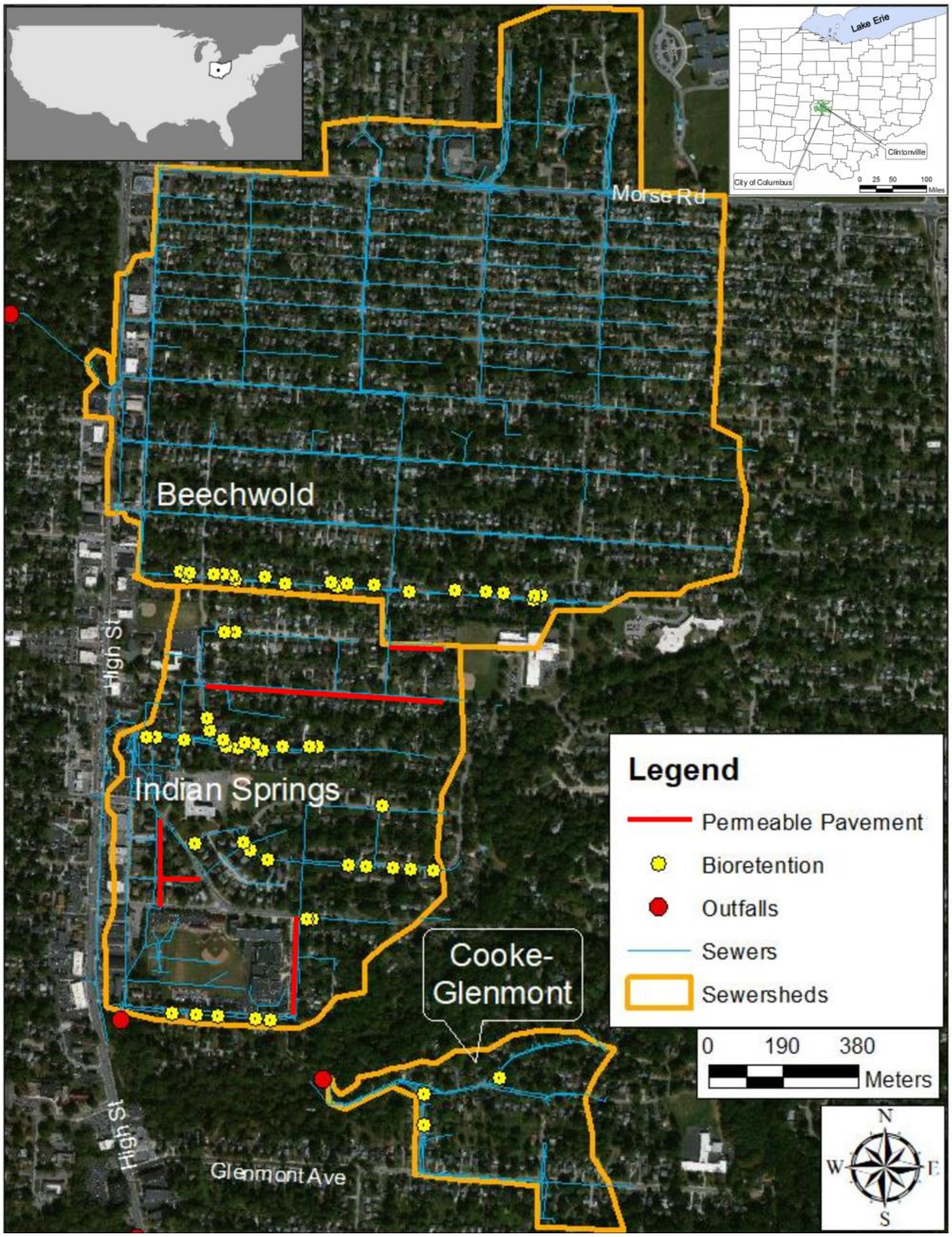

Figure 1: Map of sewersheds. Control (Beechwold) and treatment (Indian Springs and Cooke-Glenmont) sewersheds are outlined in orange. Blue lines indicate storm sewers. Red lines represent permeable pavement. Yellow dots represent bioretention cells, and red dots indicate storm sewer outfalls where sample collection occurred.

Table 1: Sewershed Characteristics

Sewershed	Area (ha)	Land Use (%)			Imperviousness (% of Total Area)	GI Surface Area (% of Sewershed Area)	% Sewershed Area Draining to Bioretention	Sewershed Storage Added by Bioretention* (mm)
		Residential	Commercial	Institutional				
Beechwold	111.5	95.7	3.6	0.7	38.2	0.0074	2.1	0.0075
Indian Springs	47.8	75	7.6	17.4	40.3	1.91	23.6	0.19
Cooke-Glenmont	11.5	100	0	0	30.9	0.38	30.1	1.63

*Land surveying was used to measure added sewershed storage from bioretention and permeable pavement in late 2019 through early 2020. Accumulated mulch and detritus since construction ended to when land surveying occurred may have occupied some of the bioretention bowl storage

The control and treatment sewersheds were located within a 1 km radius. Since the majority of the 111.5-ha Beechwold sewershed was not retrofitted (only 0.0074% of the sewershed was covered by GI on a single street), it served as the control for the experiment (Table 1). This sparse GI at Beechwold was installed the same timeline as GI at Indian Springs. Statistical testing to show this GI did not affect water quality in Beechwold, but rather sewershed and rainfall characteristics, will be presented in section 1.3.1; therefore, Beechwold is appropriate for use as a control.

Residential land use ranged from 75-100% among the sewersheds, with interspersed commercial land uses along major thoroughfares and institutional (i.e., schools) land uses (Table 1). Imperviousness ranged from 30.9% at Cooke-Glenmont, which was located in a forested area near a ravine, to 40.3% at Indian Springs. Indian Springs had the highest percentage of institutional land use (17.4%) which contributed substantial directly connected impervious areas (i.e., large roofs and parking lots). The three largest sources of imperviousness in the sewersheds were roofs (12.5-15.7%), roads (8.6-11.0%), and driveways (6.4-8.3%), respectively.

Different types and densities of GI were retrofitted into the Indian Springs and Cooke-Glenmont sewersheds. Thirty-two bioretention cells and five permeable pavement roads or alleys were constructed in the 47.8-ha Indian Springs sewershed over approximately a 1-year period. GI practices covered 1.91% of the sewershed surface area, and bioretention treated 23.6% of the sewershed area, adding 0.19 watershed millimeters of storage in the sewershed (Table 1). Cooke-Glenmont, the smallest sewershed at 11.5 ha, had two regional bioretention cells and a third cell retrofitted within its boundaries.

Taken together, this GI accounted for 0.38% of the sewershed area and treated 30.1% of its surface area. These three cells added 1.63 sewershed mm of storage.

1.2.2 GI Retrofits

Among the 32 bioretention cells at Indian Springs, 11 protruded into the street to intercept runoff along the curbline (Figure 2a). The other 21 were located behind the curb in the easement in front of houses (Figure 2b). All bioretention cells in this area were equipped with an underdrain, with a media depth of approximately 60 cm above the underdrain. The median bioretention cell surface area at Indian Springs was 8.74 m^2, treating a median drainage area of 0.26 ha. There was no internal water storage (i.e., an upturned elbow in the underdrain providing storage for inter-event exfiltration) for bioretention in this sewershed. Bioretention cells were planted with (1) grasses, especially *alamagrostis acutiflora*, *panicum virgatum*, and *pennisetum alopecuroides* (2) perennials including *asclepias tuberosa*, *iris versicolor,* and *rudbeckia fulgida*, and (3) shrubs such as *hypericum frondosum*. Indian Springs was the only sewershed where permeable pavement was installed (Figure 1; Figure 2c). Five roads or alleys were retrofitted with curb-to-curb permeable pavement with a total surface area of 8,742 m^2, representing 1.83% of the sewershed area. The typical cross section was 65-150 cm deep and given the low hydraulic conductivity of the soils in the neighborhood, an underdrain was also employed in all five permeable pavements.

At Cooke-Glenmont, regional bioretention cells were installed in series. The upstream cell had a surface area of 152.1 m^2 occupying 0.13% and treating 15.8% of the sewershed (Figure 2d). A second, larger (255.4 m^2) bioretention cell was located downstream, and treated effluent from the upstream cell (Figure 2e). It occupied 0.22% and treated a total of 24.4% of the sewershed. The smallest (28.1m^2) bioretention cell at Cooke-Glenmont occupied 0.02% and treated 5.4% of the sewershed (Figure 2f). Characteristics of the bioretention cell included 60 cm of bioretention media, 30 cm of drainage aggregate surrounding an underdrain, and 30 cm of bowl storage. Internal water storage was not employed in bioretention cells in Cooke-Glenmont. Regional bioretention cells were planted with (1) grasses and sedges, such as *panicum virgatum* and *carex morrowii*, and (2) perennials, especially *polygonatum odoratum*, *rudbeckia fulgida*, and *symphyotrichum ericoides*, Bioretention in both treatment sewersheds utilized the same media which met the state standards as defined by OEPA (2006).

Figure 2a-f: Green infrastructure practices. Bioretention (a-b) and permeable pavement (c) utilized in the Indian Springs Sewershed. Bioretention (d-f) utilized in the Cooke-Glenmont sewershed

1.2.3 Construction and Monitoring Timeline

GI construction occurred independently and on different timelines at the treatment sites (Table 2). Broadly, monitoring was divided into three phases: 1) pre-GI 2) construction and 3) post-GI. The pre-GI phase refers to the period before the construction of GI. The construction phase refers to the period during GI construction; data from this phase were not analyzed for Indian Springs, since the goal of this work was to assess pre- and post-GI differences in water quality. Post-GI refers to the period when GI facilities were brought online. Some secondary project construction (i.e., redirecting downspouts, implementing sump pumps, and lining sanitary sewer laterals) occurred at Indian Springs during the post-GI phase.

In the case of Cooke-Glenmont, pre-GI and construction phases were combined to form the “baseline” phase. The first water quality sample at Cooke-Glenmont was not collected until September 29, 2016 and the last sample before construction commenced was collected on December 6, 2016. Combining these project phases augmented the roughly two months of pre-GI data with 7.5 months of additional data, allowing for improved comparisons of changes in water quality pre- and post-GI retrofit. This larger baseline data set also allows the impacts of seasonal changes to water quality to be captured. The combination of these project phases was further justified using the Kruskal-Wallis test as presented in section 1.3.1.

During winter months, sampling equipment was removed to avoid damage to it from ice and snow. Equipment was not deployed during the following periods:

December 19, 2016 to March 19, 2017, December 6, 2017 to March 2018, and December 6, 2017 to March 20, 2018 (Table 2).

Table 2: Construction and Monitoring Timeline

	Project Phase	
Sewershed	Pre-GI/Baseline	Post-GI
Cooke-Glenmont*	9/29/2016-7/13/2017	9/14/2017-8/13/2019
Indian Springs**	9/30/2016-11/19/2017	10/29/2018-8/26/2019
	Monitoring Period	
Control	9/29/2016	12/9/2019

*Baseline phase at Cooke-Glenmont includes construction phase
**Secondary construction projects were happening at Indian Springs during post-GI

1.2.4 Experimental Design and Data Collection

This study utilized a before-after, control impact (BACI) design to determine if water quality changes were due to GI or other external factors, such as changes in climate or pollutant generation in the sewersheds (Green, 1993; Page et al., 2015; Shuster & Rhea, 2013). Water quality samples were collected before and after GI was installed at both control (Beechwold) and treatment sewershed (Indian Springs or Cooke-Glenmont) outfalls.

A 0.254-mm resolution tipping bucket (Davis Rain Collector) and a manual rain gage were deployed within or adjacent to the control and both treatment sewersheds. They were attached to a 180-cm tall wooden post in locations free from overhead obstructions. Rainfall data from the tipping bucket rain gages were stored on Hobo

Pendant data loggers (Onset Computer Corporation, Bourne, Massachusetts). Rainfall data were stored on a 1-minute interval. Readings were verified and automated sampler pacing was re-calibrated after each using manual rain gage measurements, as described below.

The Cooke-Glenmont outfall was ephemeral, while Indian Springs and Beechwold had continuous baseflow. Cooke-Glenmont and Beechwold were equipped with an area velocity meter (AVM; Teledyne Isco, Lincoln, Nebraska), which communicated with ISCO 750 module attached to an ISCO 6712 sampler. Meanwhile at Indian Springs, AVMs transmitted measurements to an ISCO 2150 flow module and data were stored on an ISCO 2100 sample interface module. These modules communicated with an ISCO 3700 series sampler. Collectively, flow modules determined flow rate on 1-minute intervals. Flow rate was integrated with time to determine runoff volume and to trigger sample aliquots obtained by automated samplers.

All composite samples were composed of a minimum of five and a maximum of 50, 200 mL aliquots describing greater than 80% of the pollutograph (U.S. EPA 2002). Composite samples were vigorously shaken within 18.9L bottles to ensure suspension of particulate matter and a well-mixed, event mean concentration (EMC). Aliquots were paced such that up to a 50-mm event could be sampled.

In a few cases (i.e., two times at Beechwold and once at Cooke-Glenmont), two composite water quality samples were obtained during a single storm event due to rainfall depth exceeding the 50-mm maximum depth When this occurred, a runoff volume weighted average concentration was used in the analysis. Because of the short antecedent dry period (six hours) used to separate rainfall events, one to three samples at each site represented the water quality of multiple hydrologic events. This occurred when the flow had not returned to baseflow before the onset of the next rainfall event, causing the samplers to combine two storms within the composite bottle. In these cases, the separate hydrologic events were combined for pollutant concentration and load analysis.

1.2.5 Data Analysis

Summary statistics for pollutant concentrations were determined using laboratory-reported EMCs. These included the number of observed events, median pollutant concentrations, and pollutant loads during each phase (i.e., baseline, pre-GI, or post-GI) for control and treatment sewersheds. Observed changes in water quality due to GI implementation were compared to other similar studies. They were also compared to influent and effluent summary statistics for individual GI practices from the International Stormwater BMP Database (Clary & Jones, 2016).

Pollutant loads from each sewershed were determined as the product of pollutant EMC and runoff volume on a storm-by-storm basis. Pollutant loads were reported on a sewershed area-normalized basis and were calculated using the following equation:

$$L_{\mathrm{i}} = 1 \times 10^{-3} \times \frac{EMC_{\mathrm{i}} \times V}{A_{WS}} \quad (1)$$

where L_i is the load of pollutant i (g/ha), EMC is the event mean concentration (mg/L), V is the runoff volume (L) measured after discounting baseflow, A_{WS} is the sewershed area (ha), and the constant converts from milligrams to grams.

Annual loading (L_m, kg/ha/month) was estimated by accounting for storms not sampled for water quality. The ratio of long-term average annual rainfall depth (RF_{LTA};

mm/yr) to total rainfall depth sampled for water quality (RF_{SAMP}; mm) was utilized to scale the annual loading (Equation 2). Thus, we assume that the sampled storm events are representative of the overall population of runoff volume and pollutant concentration. The annual loading was also normalized by sewershed area and monitoring period duration (d_{MP}, years):

$$L_a = 1 \times 10^{-3} \times \frac{\sum_{i=1}^{n}(EMC_i \times V_i) \times RF_{LTA}}{A_{WS} \times RF_{SAMP}} \quad (2)$$

where n is the number of sampled storm events. To determine the effects of different event depths on annual load, bins of event depth were created and the load within each bin was summed. This load was then scaled by the ratio of the total rainfall depth to the total sampled rainfall depth within each bin to estimate the total load by event depth bin. Annual loading was calculated by considering each project phase to be an individual monitoring period. Since water quality samples were not collected during the cold winter months, annual loading presented herein extrapolates for these months. Nitrate EMCs above 2 mg/L were assumed to be related to fertilizer application, and were removed for annual loading (Foster et al., 1982; Wakida & Lerner, 2005)

Among the three monitored sewersheds, comparisons between sampled and observed rainfall events, rainfall characteristics, pollutant concentration, and pollutant load were made to determine significant differences. The Wilcoxon rank sum test was used to determine if sampled storm event characteristics varied from those of all observed storms. Using the Kruskal-Wallis test, rainfall characteristic comparisons were made across sewersheds and across project phases. Water quality data were log transformed, after which the Shapiro-Wilk test was used to check for normality of model residuals.

When a linear relationship was present in the data, model residuals were normally distributed, demonstrated homoscedasticity, and showed no multicollinearity, analysis of covariance (ANCOVA) was used to compare treatment to control data. ANCOVA analysis was utilized to uncover significant differences in the slopes and intercepts of water quality concentration and storm event load parameters (Page et al., 2015). If the residuals were not normally distributed, yet the sample size was large (>30), parametric statistical analysis methods were still used (Ghasemi & Zahediasl, 2012) since sample sizes were large enough to approximate the population. When a significant linear relationship did not exist for water quality parameters during the pre-GI phase, but was present for the post-GI phase, a paired t-test was used to compare control and treatment sewersheds during the post-GI phase. No statistical analyses were performed on water quality data lacking either an adequate sample size or a significant linear relationship. Percent changes in pollutant concentration and storm event load were calculated and reported using least squares mean (LSM) analysis:

$$Change\ (\%) = \left(\frac{10^{\bar{Y}_{Post}}}{10^{\bar{Y}_{Pre}}} - 1\right) \times 100 \qquad (3)$$

where $\bar{Y}_{Post}$ is the treatment sewershed LSM during the post-GI phase, and $\bar{Y}_{Pre}$ is the treatment sewershed LSM during the pre-GI phase. Herein, percent concentration and storm event load percent differences observed after the adoption of GI refer to the LSM percent difference. On the other hand, the percent difference between annual load by project phase is simply reported as percent change (since annual load is a single value, not a distribution that can be statistically tested). All stormwater data analysis was completed using R statistical software version 3.4.2 (R Core Team 2018). Except where noted, a criterion of 95% confidence (α=0.05) was used.

1.2.6 Laboratory Techniques

After fully suspending particulate pollutants, composite samples were divided among a 500-mL pre-acidified bottle for total ammoniacal nitrogen (TAN; e.g., the amount of ammonia in the sample), total Kjeldahl nitrogen (TKN), and nitrite (NO_2) analysis, a 500mL bottle for nitrate (NO_3) and TSS analysis, and a 60mL bottle (following field filtration through a Whatman Puradisc 0.45 µm filter) for orthophosphate (OP) analysis. Samples were collected within 24 hours after the cessation of rainfall, placed on ice (<4ºC), and transported to the laboratory.

Total nitrogen (TN), organic nitrogen (ON), and particle-bound phosphorus (PBP) were calculated using methods in Table 3. Nitrate-nitrate (NO_{2-3}) concentrations were calculated as the sum of nitrate and nitrite concentrations for each sampled event. Samples were analyzed using either U.S. EPA (1983) or American Public Health Association (APHA et al. 2012) methods. A value of one-half the detection limit was substituted for EMCs below the method detection limit (MDL; Antweiler and Taylor 2008). Analytes exhibiting a moderate amount of BDL concentrations (i.e., 10-35% of sampled events) were: OP at Indian Springs (17.2% BDL); TP at and Indian Springs (20.0% BDL); and TSS at all three sewersheds (Beechwold 15.2% BDL; Cooke-Glenmont 10.8% BDL; Indian Springs 25.0% BDL). For all other analytes, BDL concentrations were observed for fewer than 10% of sampled storm events. All concentrations above MDL were analyzed without transformation.

Table 3: Laboratory Methods, Preservation Procedure, and Method Detection Limit for Nutrients and Sediment

Parameter	Abbreviation	Laboratory Method	Preservation	MDL (mg/L)
Total Kjeldahl Nitrogen	TKN	EPA Method 351.21	H_2SO_4 (<2 pH), <4˚C	0.078
Nitrite	NO2	EPA Method 353.2	H_2SO_4 (<2 pH), <4˚C	0.018
Nitrate	NO3	EPA Method 353.2	<4˚C	0.043
Total Nitrogen	TN	Calculated TKN + NO_2 + NO_3	NA	NA
Total Ammoniacal Nitrogen	TAN	EPA Method 350.1	H_2SO_4 (<2 pH), <4˚C	0.0031
Organic Nitrogen	ON	Calculated as TKN-TAN	NA	NA
Orthophosphate	OP	EPA Method 365.2	<4˚C	0.01
Particle-bound Phosphorus	PBP	Calculated as TP-OP	NA	NA
Total Phosphorus	TP	EPA Method 365.2	<4˚C	0.1
Total Suspended Solids	TSS	Standard Methods 2540D2	<4˚C	2

1.3. Results and Discussion

1.3.1 Justification of Experimental Setup

Following the same timeline as Cooke-Glenmont for baseline and post-GI phases, a significant difference in TAN concentration was observed at Beechwold (p<0.05). TAN concentrations have been shown to exhibit variability based on anthropogenic activities and microbes in lawns (Parkin, 1987; Raciti et al., 2011). For these reasons, and given GI only covered 0.0074% of the surface area at Beechwold, GI installation was likely not the reason the significant difference in TAN observed at Beechwold. Further, following the same timeline as Indian Springs for pre- and post-GI phases, a significant different in TSS concentration was observed at Beechwold (p<0.05). Rather than the implementation of sparse GI at Beechwold during the same time as Indian Springs, this TSS difference was likely due to the disparity in 5-minute peak rainfall intensity observed across project phases (p<0.05; more discussion of rainfall characteristics to follow in section 1.3.2). During the time frames corresponding with pre- and post-GI phases at Indian Springs, median 5-minute peak rainfall intensities for sampled events at Beechwold were 22.1 and 13.0 mm/hr, respectively. Past studies have shown high rainfall intensities to drive TSS due to sediment erosion (Sharma et al., 2016). Since GI installed at Beechwold only treated 2.1% of the sewershed surface area and no other water quality parameters exhibited significant differences with project phase, Beechwold was used for the control.

Combining the pre-GI and construction phases at Cooke-Glenmont to create the baseline phase increased the data set from roughly two to 9.5 months (n = 7 to 25 storms), which resulted in a more robust dataset to compare with post-GI. Only two pollutants exhibited a significant difference in pollutant concentrations between the pre-GI and construction phases: TAN and OP ($p<0.05$). TAN and OP are primarily dissolved pollutants, and past studies attributed seasonal changes in these pollutants to the breakdown of organic material and seasonal mineralization (Hathaway et al., 2012; Yang & Toor, 2018). The observed difference in these pollutants is likely due to these seasonal differences rather than construction activities; we would not expect construction of SCMs to release TAN or OP, but rather TSS and associated particulate-bound pollutants (Alsharif, 2010; Atasoy et al., 2006; Müller et al., 2020). For all other pollutants, no significant difference in concentration was observed between pre-GI and construction project phases. For this reason, pre-GI and construction phases at Cooke-Glenmont were combined to form the "baseline" Phase.

1.3.2 Characteristics of Sampled Events

At Beechwold, Cooke-Glenmont, and Indian Springs, 102, 67, and 40 storm events, respectively, were sampled for water quality during the monitoring period or project phases as described in Table 1. During these periods, storm events sampled for water quality represented 39.1-67.5% of the total rainfall. The median event depth for sampled storms ranged from 14-16.8 mm across the sewersheds, slightly greater than the median event depth for observed storms of 9.7-10.4 mm. This can be attributed to minimum sample volumes required for laboratory analyses, which precluded the analysis of storms less than 3 mm. The median 5-minute peak rainfall intensity for sampled storms, which ranged between 13.7 and 18.3 mm/hr across the sewersheds, was similar to the median peak intensity recorded for all observed storms (13.7-15.2 mm/hr). The median ADP for sampled events (2.7-3.7 days) was similar to the median ADPs determined from all observed events in the sewersheds (3.1-3.3 days).

The Wilcoxon rank sum test showed a significant difference existed between observed and sampled storms for rainfall depth (p<0.001), but no significant differences existed for other rainfall characteristics (i.e. average intensity, peak 5-minute intensity, ADP, and rainfall duration). From these results, we can conclude that the sampled storm events were representative of the overall distribution of storms observed in the sewersheds during the monitoring period. Furthermore, no significant difference in the previously mentioned rainfall characteristics existed between pre- and post-GI phases at Indian Springs, and between baseline and post-GI phases at Cooke-Glenmont, except for 5-minute peak rainfall intensity (p<0.05). Generally, median 5-minute peak intensities during the baseline or pre-GI phase (16.8-22.9 mm/hr) were greater than the post-GI phase (10.7-13.7 mm/hr) for sampled events.

Results from Kruskal-Wallis k-sample tests showed that rainfall characteristics did not significantly differ between the three sewersheds (p>0.68 in all cases; Kruskal & Wallis, 1952). This is logical as the sewersheds are within 1 km of each other.

1.3.3 Nitrogen

The median concentration of TAN at Cooke-Glenmont was reduced by 64.0%, from 0.122 to 0.062 mg/L, with the installation of GI (p<0.001; Table 5). A 67.7% reduction in TAN load was also observed at Cooke-Glenmont (p<0.001), where the median storm event load decreased from 5.62 to 2.38 g/ha. The aerobic environment within the porous bioretention media promoted nitrification, where TAN was biologically oxidized to NO_2 and further oxidized to NO_3 (Hunt et al. 2012; Wang et al. 2017; Osman et al. 2019). The significant reduction in TAN concentrations and increase in NO_3 concentrations (by 5.9%) supports the occurrence of nitrification within bioretention at Cooke-Glenmont. Data in the International Stormwater BMP Database supported nitrification in individual bioretention cells, with the median NO_3 concentration increasing from 0.35 mg/L to 0.48 mg/L through bioretention cells (Clary & Jones, 2016). Other sewershed-scale studies also demonstrated nitrification in GI, with TAN concentrations and storm event loads decreasing 19-71%, and concurrent NO_3 concentrations and storm event loads either not changing significantly or increasing up to 100% (p<0.05; Bedan & Clausen, 2009; Page et al., 2015).

Table 4: Summary statistics for concentrations and storm event loads of nitrogen by project phase at Cooke-Glenmont (CG) and Indian Springs (IS). Interpretations related to project phase were made using an ANCOVA. Comparisons to the control were done using a t-test on the post-GI data only.

	Pollutant	Site	Baseline or Pre-GI Phase			Post-GI Phase			Statistical Results			
			n	Control Median	Treatment Median	n	Control Median	Treatment Median	LSM % Difference	t-value	p-value	Interpretation
Concentration (mg/L)	TAN	CG	20	0.11	0.122	47	0.078	0.062	-64.0	-4.02	1.55E-04	Baseline > Post-GI
		IS	22	0.085	0.19	18	0.048	0.068	-60.5	-1.04	0.305	NSD btw. phases
	TKN	CG	18	1.25	1.54	44	0.99	1.20	-14.1	3.19	0.002	Baseline > Post-GI
		IS	21	0.94	1.1	16	1.06	1.00	-16.5	-1.37	0.192	NSD btw. phases
	ON	CG	15	1.11	1.44	41	0.94	1.18	-19.6	3.17	0.003	Baseline > Post-GI
		IS	18	1.09	0.89	16	1.00	0.82	3.1	-0.94	0.352	NSD btw. phases
	Nitrate	CG	10	0.63	0.58	32	0.78	0.63	5.9	-	-	-
		IS	13	0.56	0.99	16	0.81	0.82	-22.7	-	-	-
	TN	CG	17	1.7	2.35	44	1.8	1.88	-13.7	3.16	0.002	Baseline > Post-GI
		IS	21	1.74	1.91	18	1.94	1.81	-24.1	-	-	-
Load (g/ha)	TAN	CG	16	5.55	5.62	47	2.30	2.38	-67.7	-4.55	2.67E-05	Baseline > Post-GI
		IS	19	3.12	8.7	16	2.33	5.44	-47.1	1.6	0.118	NSD btw. phases
	TKN	CG	15	56	42.6	44	49.3	52.7	-20.9	-3.0	0.004	Baseline > Post-GI
		IS	19	54.9	81.8	14	50.4	62.8	-19.9	-	-	-
	ON	CG	13	49.3	46	41	46	48.2	-25.5	-2.86	0.006	Baseline > Post-GI
		IS	17	46	37	14	46	54.9	-2.4	-	-	-
	Nitrate	CG	9	41.5	16.8	32	23.5	20.2	7.7	-1.07	0.292	NSD with control
		IS	13	13.5	19.1	14	20.2	32.5	-3.0	-	-	-
	TN	CG	14	84.1	77.3	44	65.0	63.9	-24.0	-3.0	0.004	Baseline > Post-GI
		IS	18	60.5	113.2	16	65.0	103.1	-25.4	-	-	-

Note: NSD implies no significant difference, while dash (-) indicates that statistical analyses were not performed due to insufficient sample size or data failing to meet model assumptions, negative LSM % differences imply reduction. TAN stands for total ammoniacal nitrogen, TKN for total Kjeldahl nitrogen, ON for organic nitrogen, and TN for total nitrogen

Similar to Cooke-Glenmont 60.5 and 47.1% reductions in TAN concentration and storm event load, respectively, were observed at Indian Springs following the installation of GI. The median concentration decreased from 0.190 to 0.068 mg/L, while the median storm event load decreased from 8.70 to 5.44 g/ha (Table 5). Along with bioretention, permeable pavement practices in the Indian Springs sewershed allowed for nitrification due to the aerobic environment in the pavement subsurface (Collins et al., 2010; Tota-Maharaj & Scholz, 2010). The International Stormwater BMP Database also offers support of nitrification in this practice, as the median NO_3 concentrations increased from 0.59 to 1.36 mg/L from influent to effluent.

NO_3 concentrations varied such that statistical analyses could not be performed for either treatment sewershed. At Cooke-Glenmont and Indian Springs, respectively, a 5.9% increase and 22.7% reduction in median NO_3 concentration was observed following the installation of GI (Table 5). Again, statistical analyses could not be performed for NO_3 storm event loads at Indian Springs, however, median NO_3 storm event loads at Cooke-Glenmont demonstrated no significant difference from those at Beechwold during the post-GI phase ($p>0.25$). Given the substantial TAN reductions at both treatment sewersheds through increased nitrification within GI, no significant NO_3 increases implies denitrification occurred. Since an internal water storage zone (IWS) or other restrictions to drainage is needed to promote anaerobic conditions and subsequent denitrification in GI (Hsieh et al., 2007; Page et al., 2015), and GI in treatment sewersheds lacked an IWS, denitrification likely occurred elsewhere in the sewershed. Denitrification occurs in suburban lawn soils and is highly dependent on soil moisture and available NO_3 and oxygen (Raciti et al., 2011). Perhaps differences in antecedent dry period before storm events caused variable soil moisture, which in turn, led to variable denitrification. Particulate organic matter, which is highly variable in soil, has also been shown to influence the variability of natural denitrification rates (Parkin, 1987). Though minor, NO_3 plant uptake could have also contributed to the variability of nitrification (Collins et al., 2010). It is anticipated that NO_3 uptake by the bioretention cells in the treatment sewersheds will improve as the plant roots and microbial communities become more established in the systems (Hopkinson & Giblin, 2008).

TKN concentrations and storm event loads significantly decreased by 14.1% and 20.9%, respectively, at Cooke-Glenmont ($p<0.005$), and 16.5 and 19.9%, respectively at Indian Springs with the installation of GI (Table 5). At Cooke-Glenmont, the median TKN concentration was 1.54 mg/L during the baseline phase and 1.20 mg/L during the post-GI phase. The pre- and post-GI TKN concentrations at Indian Springs were 1.10 and 1.00 mg/L, respectively. Further TKN reduction are unlikely since the International Stormwater BMP Database reported median TKN effluent concentrations of 1.39 and 1.00 mg/L for single bioretention cells and permeable pavement, respectively (Clary & Jones, 2016). Perhaps continued TKN reduction at Indian Springs was due to the adoption of both bioretention and permeable pavement at Indian Springs. Permeable pavement has been shown to remove TKN through filtration and sedimentation (Winston et al., 2016a).

Since ON encompassed 92.8% of TKN at Cooke-Glenmont, ON reductions were similar to those of TKN. ON concentration decreased 19.6% ($p<0.005$), from a median of

1.44 to 1.18 mg/L, and storm event load decreased by 25.5% ($p<0.01$) between the baseline and post-GI phases at Cooke-Glenmont (Table 5). Particulate ON removal has been shown to occur in bioretention primarily through sedimentation and filtration processes (Li & Davis, 2014). Page et al. (2015), also saw significant, 62% and 79% decreases in TKN concentrations and loads, respectively, with the installation of GI, attributing this change to ON retention by bioretention. At Indian Springs, ON concentrations and storm event loads changed by less than 5% (3.2 and -2.4%, respectively). ON made up 82% of TKN at Indian Springs. Nitrification was likely the cause of TKN, but not ON, reduction. Perhaps this difference in ON mitigation between treatment sewersheds is related to sewershed characteristics. While Cooke-Glenmont had the least imperviousness and most woody vegetation, Indian Springs had the opposite. Having more impervious surfaces and less plant life decreased the availability of ON at Indian Springs. This is supported by lower ON concentrations at Indian Springs, 0.89 and 0.82 mg/L for pre- and post-GI, respectively, than at Cooke-Glenmont, 1.44 and 1.18 mg/L for baseline and post-GI, respectively.

TN concentrations were significantly ($p<0.005$) reduced by 13.7% between the baseline and post-GI phases at Cooke-Glenmont, with the median concentration decreasing from 2.35 to 1.88 mg/L (Table 5; Figure 3). Similar to concentrations, TN storm event loads were significantly reduced (by 24.0%) at Cooke-Glenmont, with median storm event loads decreasing from 77.3 to 63.9 g/ha ($p<0.005$). Bioretention is likely responsible for TN removal here. No difference was observed in the ANCOVA slopes for TN concentration or storm event load at Cooke-Glenmont (Figure 3), meaning bioretention exhibited similar TN removal for small and large storm events. Other studies have demonstrated TN reduction through bioretention, as nearly three-hundred storms from the International BMP database showed a median TN concentration reduction from 1.24 to 1.04 mg/L as runoff passed through single bioretention cells (Clary & Jones, 2016). Since median TN concentrations during the post-GI phase (1.88 and 1.81 mg/L for Cooke-Glenmont and Indian Springs, respectively) were higher than that for effluent from single bioretention in the BMP database (1.04 mg/L), further TN reduction is possible, perhaps through an IWS zone. A study of residential sewershed-scale GI found the concentration and load of TN reduced by 58 and 79%, respectively with the adoption of GI (Page et al., 2015). Nitrification, sedimentation, and filtration were the main mechanisms of TN conversion and reduction at Cooke-Glenmont. TAN was converted to NO_3 in the aerobic soil media, and TKN was removed as particulates settled in bioretention. TN concentration and storm event load reductions between the pre- and post-GI phases at Indian Springs, 24.1% and 25.4%, respectively, were similar to those at Cooke-Glenmont. Permeable pavement likely utilized filtration and sedimentation to contribute to TN reductions.

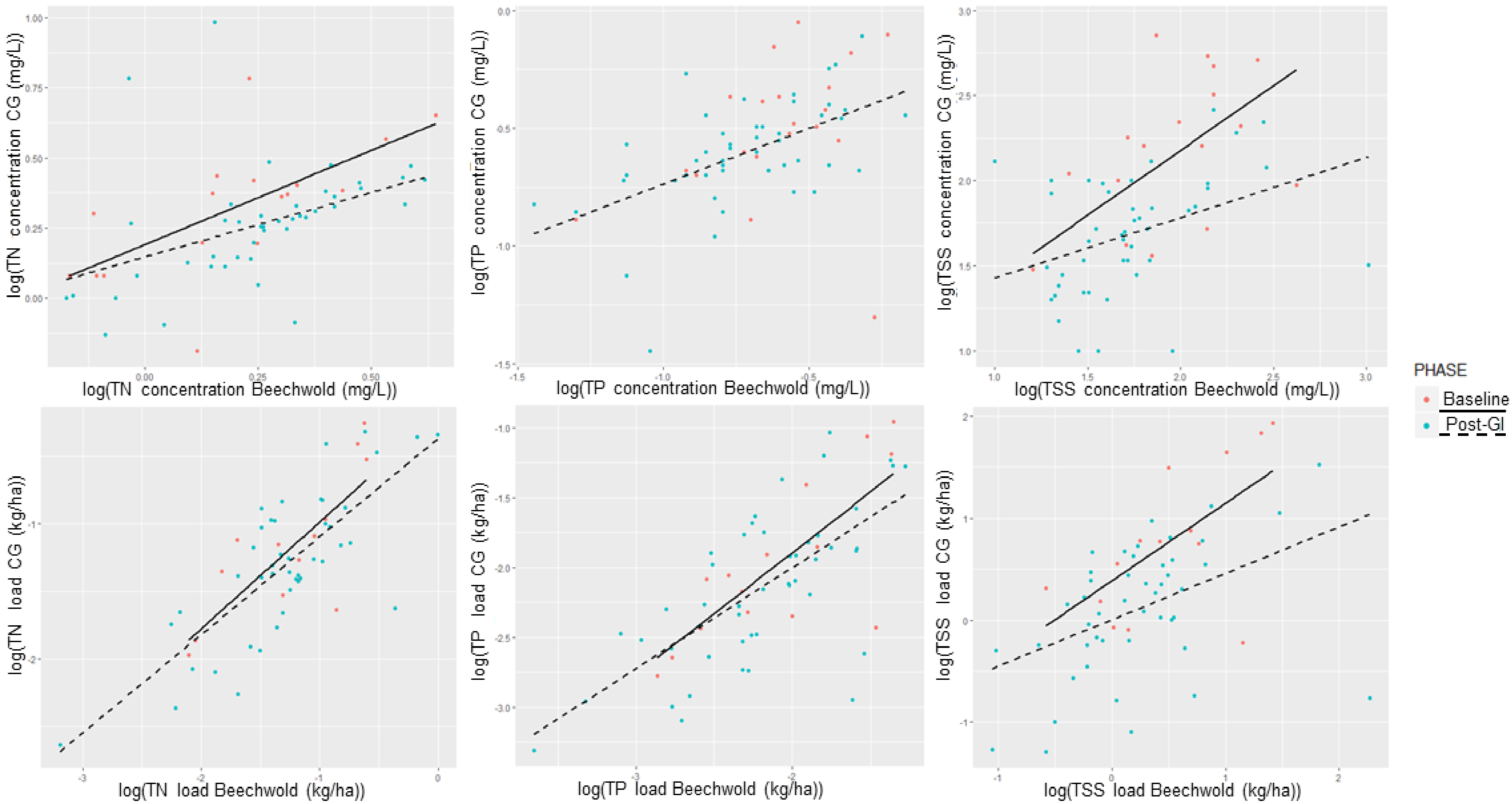

Figure 3: ANCOVA models for total nitrogen (TN), total phosphorus (TP), and total suspended solids (TSS) concentrations and storm event loads at Cooke-Glenmont. Baseline TP concentrations did not fit a linear model. For all cases except TP concentration and TSS storm event load, significant differences were observed in the intercepts ($p<0.05$). A significant difference was only observed in the slopes for TSS concentration and storm event load ($p<0.005$).

1.3.4 Phosphorus

OP is the biologically available form of phosphorus that causes eutrophication in natural water bodies (Correll, 1998). OP accounted for 44-59% of TP at each sewershed. Although insignificant, median OP concentrations and storm event loads increased marginally, by 23.7 and 18.1%, respectively at Cooke-Glenmont (Table 5). The International Stormwater BMP Database also showed an increase in OP concentrations as runoff passes through bioretention, with influent to effluent concentrations increasing from 0.02 to 0.27 mg/L (Clary & Jones, 2016). Phosphorus leaching has been observed in column studies (Bratieres et al., 2008; Palmer et al., 2013) and street-side bioretention (Chapman & Horner, 2010) in urban areas as it is leached from organic matter, typically compost, as the stormwater passes through the media. OP concentration increases have also been attributed to grass mowing and decomposition of organic matter in bioretention (Passeport et al., 2009). OP storm event load at Cooke-Glenmont during the post-GI phase showed no significant difference from Beechwold ($p > 0.1$).

Table 5 Summary statistics for concentrations and storm event loads of phosphorus by project phase at Cooke-Glenmont (CG) and Indian Springs (IS). Interpretations related to project phase were made using an ANCOVA. Comparisons to the control were done using a t-test on the post-GI data only.

	Pollutant	Site	Baseline or Pre-GI Phase			Post-GI Phase			Statistical Results			
			n	Control Median	Treatment Median	n	Control Median	Treatment Median	LSM % Difference	t-value	p-value	Interpretation
Concentration (mg/L)	OP	CG	11	0.12	0.14	30	0.11	0.13	23.7	1.59	0.123	NSD with control
	OP	IS	14	0.11	0.09	15	0.11	0.07	-25.2	-5.68	5.68E-06	Pre-GI > Post-GI
	PBP	CG	19	0.21	0.23	39	0.16	0.21	-30.9	2.83	0.007	CG > Control
	PBP	IS	19	0.15	0.2	14	0.11	0.06	-66.5	-	-	-
	TP	CG	20	0.26	0.32	47	0.19	0.25	-20.9	3.34	0.002	CG > Control
	TP	IS	22	0.24	0.20	18	0.23	0.11	-47.4	-	-	-
Load (g/ha)	OP	CG	10	5.01	2.08	29	3.47	2.93	18.1	0.29	0.776	NSD with control
	OP	IS	13	2.45	4.15	13	2.06	2.02	-46.9	-	-	-
	PBP	CG	14	6.36	7.85	37	5.53	7.13	-40.3	-1.75	0.086	Baseline > Post-GI*
	PBP	IS	14	5.04	9.76	12	4.74	3.77	-49.2	-	-	-
	TP	CG	15	7.76	9.24	47	6.66	8.34	-32.6	-2.11	0.039	Baseline > Post-GI
	TP	IS	18	6.56	8.36	16	7.78	9.47	-27.8	-	-	-

Note: Asterisk (*) indicates significance at $p<0.10$, NSD implies no significant difference, while dash (-) indicates that statistical analyses were not performed due to insufficient sample size or data failing to meet model assumptions. OP stands for orthophosphate, PBP for particle-bound phosphorus, and TP for total phosphorus, negative LSM % differences imply reduction

OP concentrations significantly decreased by 25.2% at Indian Springs with the installation of GI (p<0.001; Table 5; Figure 4). Here, the median OP concentrations decreased from 0.09 to 0.07 mg/L between the pre- and post-GI phases, while the control site remained unchanged at 0.11 mg/L. This OP reduction is likely caused by sorption to silt, clay, and organic matter (i.e., OP removal) and vegetative uptake within the bioretention practices (Davis et al., 2006; Roy-Poirier et al., 2010). Permeable pavement, which has been shown to export less pollutants (including phosphorous) than traditional asphalt, may also have contributed to the reduction in OP in the Indian Springs sewershed (Bean et al., 2007).

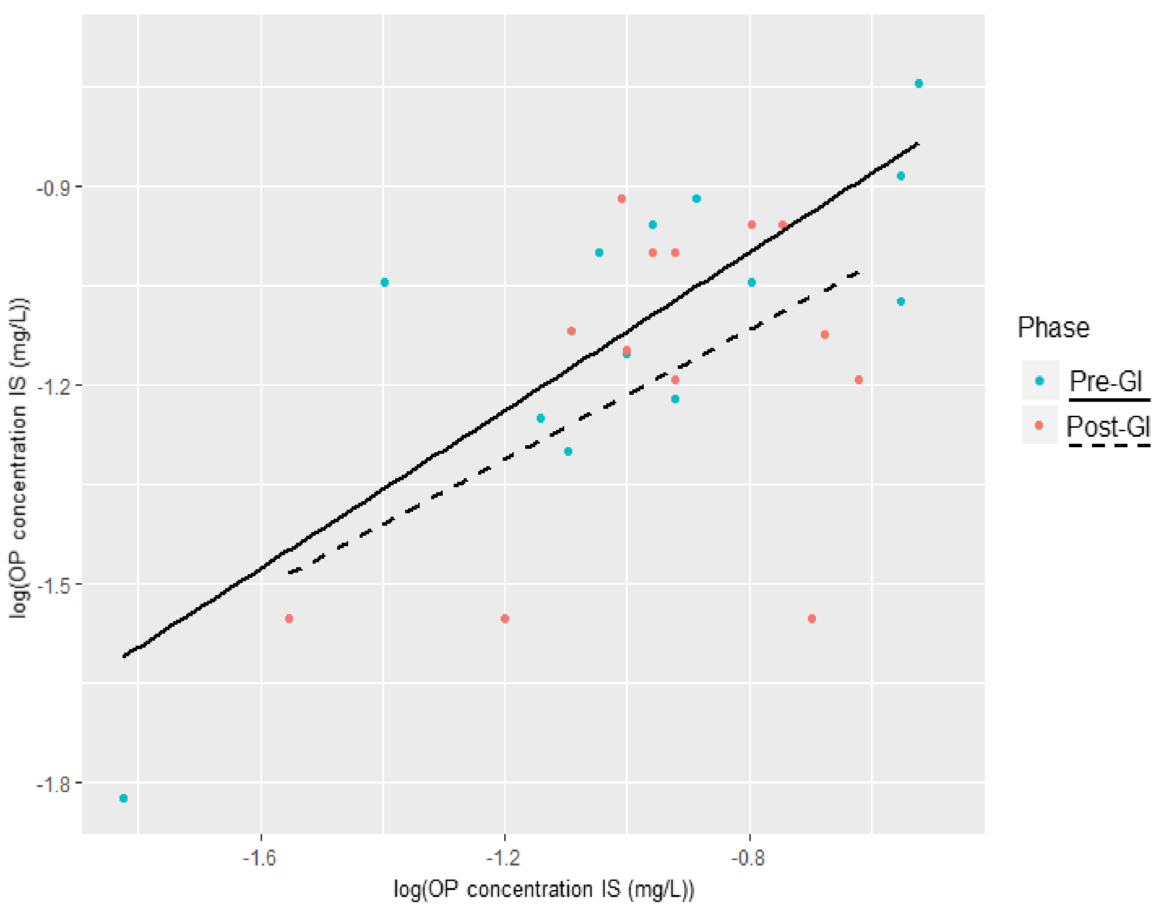

Figure 4: Orthophosphate (OP) concentration reduction at Indian Springs. A significant difference was observed between pre- and post-GI phases (*p*<0.001).

Since the same soil media was utilized in bioretention at Cooke-Glenmont and Indian Springs, the OP increases at the former and decrease at the latter must be related to hydrology and GI. Perhaps runoff flows through bioretention at different rates at both treatment sewersheds. Higher OP removal has been shown in bioretention with slower infiltration rates (Li & Davis, 2016). Perhaps runoff through bioretention at Indian Springs has a lower infiltration rate than that at Cooke-Glenmont. Also, perhaps OP leaching is due to bioretention age. A past study of OP leaching from bioretention compost found mineralization was more likely to occur in younger compost (6-months old) than older compost (24 months old; Mullane et al., 2015). Indian Springs is more similar to the younger compost as bioretention at the site was installed one-year before Cooke-Glenmont. For this reason, mineralization, or the conversion of OP to inorganic phosphorus, likely occurred with younger bioretention cells at Indian Springs.

PBP concentrations were significantly greater at Cooke-Glenmont than Beechwold ($p<0.01$; Table 5). This is likely due to the sewershed characteristics, where Cooke-Glenmont represented a more woody, vegetated area than Beechwold (Figure 1). Wooded sewersheds deliver elevated phosphorus concentrations and loads because of leaf detritus and soil erosion (Gulis & Suberkropp, 2003; Lusk et al., 2020). PBP concentrations and storm event loads ($p<0.1$) were reduced by 30.9% and 40.3%, respectively, between the baseline and post-GI phases at Cooke-Glenmont. Observed PBP reductions may be due to sedimentation and filtration within the bioretention cells (Roy-Poirier et al., 2010). PBP concentrations and storm event loads were reduced by 66.5% and 49.2%, respectively, in the Indian Springs sewershed following the installation of GI (enough data have not been collected to date to test for significance). Similar to bioretention processes, permeable pavement has been effective in settling and filtering particulate phosphorus (Winston, et al., 2016).

TP concentrations were significantly higher at Cooke-Glenmont than Beechwold ($p<0.005$). Again, this is likely due to the land cover characteristics in the sewershed, where Cooke-Glenmont had substantial forested cover (Figure 1). TP concentrations and storm event loads ($p<0.05$) decreased by 20.9% and 32.6%, at Cooke-Glenmont, and 47.4% and 27.8% at Indian Springs, respectively, with the adoption of GI (Table 5). Since a significant reduction in TP storm event load was observed at Cooke-Glenmont with the installation of GI, PBP sedimentation offset the marginal OP increase at that site. No significant difference existed in the ANCOVA slopes for TP storm event load at Cooke-Glenmont (Figure 3), meaning bioretention exhibited similar TP removal for small and large storm events. Median TP concentrations for Cooke-Glenmont and Indian Springs during the post-GI phase (0.25 and 0.11 mg/L, respectively), were comparable to median TP effluent concentrations from single bioretention and permeable pavement (0.24 and 0.11 mg/L, respectively; Clary & Jones, 2016). This implies further TP reductions through GI practices are unlikely. Past residential and commercial GI studies demonstrated TP concentration and load reductions in the range of 29-72% (Line et al., 2012; Page et al., 2015). These reductions were due to a combination of adsorption of dissolved phosphorus and sedimentation of particulate phosphorus in bioretention (Hsieh & Davis, 2005; Roy-Poirier et al., 2010a).

1.3.5 Total Suspended Solids

TSS concentrations decreased by 61.6%, from 160 to 49 mg/L, at Cooke-Glenmont with the installation of GI (p<0.001). A 78.3% reduction in TSS storm event load was observed at Cooke-Glenmont. ANCOVA analysis for this sewershed revealed that the difference in intercepts were not significant (p>0.5), but slopes were significantly different between the baseline and post-GI periods for TSS storm event loads (p<0.005; Figure 3). This implies that bioretention at Cooke-Glenmont may be better suited for reducing TSS storm event loads for smaller storm events. TSS concentration decreased 61.6% between the pre- and post-GI phases at Indian Springs, with median concentrations changing from 83 to 20 mg/L, and TSS storm event load decreasing by 59.5% with the installation of GI (Table 6). Median TSS concentrations during the post-GI phase at both treatment sites (49 and 20 mg/L for Cooke-Glenmont and Indian Springs, respectively), were larger than those reported by the International Stormwater BMP Database for effluent from single bioretention cells and permeable pavement (10.0 and 26.0, respectively; Clary & Jones, 2016). This implies further TSS reduction is possible through GI. While a reduction in TSS concentration was observed at Beechwold during the time frame corresponding to pre- and post-GI phases at Indian Springs (p<0.05; due to a significant difference in peak 5-minute as described in sections 1.3.1 and 1.3.2), the LSM percent difference accounts for it. For this reason, substantial reductions in TSS concentrations and storm event loading were observed at Indian Springs beyond the reductions observed at Beechwold. Since 30.1% and 23.6% of Cooke-Glenmont and Indian Springs, respectively, were treated by bioretention, yet 61.6-

67.7% TSS concentrations reductions were observed, this implies excellent TSS removal. Sedimentation and sediment retention within bioretention cells have shown to effectively decrease TSS concentrations, at times by several orders of magnitude (Trowsdale & Simcock, 2011). In addition to the bioretention, permeable pavement at Indian Springs likely contributed to the decrease in TSS concentration through sedimentation and filtration (Brown et al., 2009). Other residential and commercial GI studies reported significant differences in TSS concentration; Page et al (2015) reported an 82% decrease from 54 to 7 mg/L, and Line et al. (2012) reported a 99% decrease from 65 to 19 mg/L.

Table 6: Summary statistics for concentrations and storm event loads of total suspended solids (TSS) by project phase at Cooke-Glenmont (CG) and Indian Springs (IS). Interpretations related to project phase were made using an ANCOVA.

	Site	Baseline or Pre-GI Phase			Post-GI Phase			Statistical Results			
		n	Control Median	Treatment Median	n	Control Median	Treatment Median	LSM % Difference	t-value	p-value	Interpretation
Concentration (mg/L)	CG	19	74	160	46	49	49	-61.59	4.2	8.59E-05	Baseline > Post-GI*
	IS	18	51	83	18	30	20	-67.66	-	-	-
Load (kg/ha)	CG	14	3.23	6.47	46	1.69	1.68	-78.29	-0.09	0.926	NSD btw. Phase*
	IS	15	2.07	3.74	16	1.33	1.43	-59.52	-	-	-

Note: NSD implies no significant difference, while dash (-) indicates that statistical analyses were not performed due to insufficient sample size or data failing to meet model assumptions. * indicates a significant difference was observed in ANCOVA slopes, whereas the p-value indicates a significant difference in ANCOVA intercepts.

1.3.6 Annual Loading

Measured loads from each treatment sewershed were annualized (kg/ha/yr) and compared to those from the control sewershed as well as similar studies from the literature (Table 7). Annual TAN loads decreased by 71.9 and 68.7% at Cooke-Glenmont and Indian Springs, respectively; therefore, GI density did not appear to have a substantial impact on TAN annual load reductions. Rather, added GI in sewersheds added more space for nitrification. These reductions were similar to the 80-87% TAN annual load reductions reported by other residential and commercial GI studies (Line et al., 2012; Page et al., 2015). Baseline or pre-GI annual TAN loads of 1.47-2.46 kg/ha/yr were similar to the 1.7 kg/ha/yr reported for residential stormwater runoff (Line et al., 2002). During the post-GI phase, annual loads of 0.41-0.77 kg/ha/yr were similar to the post-GI phase of other LID studies (0.0-0.23 kg/ha/yr; Line et al., 2012; Page et al., 2015) and Beechwold (0.51 kg/ha/yr).

Table 7. Annual nutrient and sediment pollutant load (kg/ha/year) for sewersheds by project phase.

	Beechwold	Cooke-Glenmont			Indian Springs			Page et al (2015)			Line et al (2012)		
Pollutant	Control	Baseline	Post-GI	% Diff	Pre-GI	Post-GI	% Diff	SCM Calibration	SCM Treatment	% Diff	NoTreat	LID	% Diff
TAN	0.51	1.47	0.41	-71.9	2.46	0.77	-68.7	0.2	0.0	-80	1.54*	0.23*	-87
TKN	5.12	10.01	7.03	-29.8	19.85	7.92	-60.1	2.6	0.5	-81	5.46	1.51	-74
$NO_{2,3}$-N	1.06	1.35	0.98	-27.6	6.26	1.31	-79.1	0.3	0.1	-60	1.41	2.72	176
TN	7.89	13.89	8.72	-37.2	29.07	11.49	-60.5	2.9	0.6	-79	6.87	4.29	-42
OP	0.72	0.97	1.19	22.1	1.48	0.45	-69.7	0.3	0.1	-55	0.05	0.05	-
PBP	0.65	2.17	0.88	-59.7	4.07	1.37	-66.4	-	-	-	-	-	-
TP	0.83	2.62	1.26	-51.9	4.19	1.12	-73.3	0.7	0.6	-11	0.42	0.24	-54
TSS	525	2114	343	-83.8	5198	242	-95.3	157	12	-92	244	8	-97

Note: % Diff refers to the percent difference in annual pollutant load between baseline or pre-GI and post-GI phases. This difference is an arithmetic difference, not LSM

* as NH_3-N

$NO_{2,3}$ annual loads decreased by 27.6 and 79.1% at Cooke-Glenmont and Indian Springs, respectively (Table 7). These reductions likely occurred because GI could allow a place for denitrification, however, an IWS is usually required for this. Differences between treatment sewersheds in $NO_{2,3}$ annual loads reductions could be related to hydraulic retention time or sewershed characteristics. Perhaps GI at Indian Springs had a longer hydraulic retention time, thereby allowing for more contact time for denitrification in GI. Also, perhaps anthropogenic and soil characteristics at Indian Springs created an environment needed for denitrification (i.e., moist soil, ample nitrate, oxygenated soil). Past studies on residential GI implementation reported highly variable $NO_{2,3}$ annual load reductions. Whereas Page et al. (2015) reported a 60% decrease from treating 91% of the residential sewershed drainage area with GI, Line et al. (2012) reported a 176% increase in $NO_{2,3}$ annual load while treating runoff from a parking lot. This implies that a parking lots is not a suitable place for denitrification as it does not provide appropriate conditions. In this sense, Cooke-Glenmont should be better equipped for denitrification because it has a smaller percent imperviousness than Indian Springs, but perhaps anthropogenic activities in Indian Springs provide the $NO_{2,3}$ required for denitrification

TKN annual loading decreased by 29.8 and 60.1% post-GI at Cooke-Glenmont and Indian Springs, respectively (Table 7). Although GI at Indian Springs treated a smaller percentage of the watershed, annual TKN loading decreased substantially more than that of Cooke-Glenmont. Perhaps this discrepancy is due to sewershed characteristics. Since Cooke-Glenmont is heavily forested, more ON may be coming from the untreated portions of the sewershed. Therefore, TKN annual loads at Cooke-

Glenmont would be sustained by organic matter from this wooded area. Other residential GI studies which implemented both bioretention and permeable pavement and located in residential areas with less forested cover reported TKN annual loading reductions similar to that of Indian Springs (74-81%; Line et al., 2012; Page et al., 2015).

Annual TN loading decreased by 37.2% at Cooke-Glenmont and 60.5% at Indian Springs (Table 7). These TN reductions were due to the nitrogen conversions and reductions resulting from nitrification, sedimentation, filtration within GI, and seldom denitrification in GI, or more frequently in other areas of the sewersheds. A lesser annual TN load likely occurred at Cooke-Glenmont because organic matter from areas not treated by GI likely sustained TKN mass export. Further, perhaps longer hydraulic loading times and anthropogenic sources at Indian Springs fueled denitrification.

Annual OP load increased by 22.1% at Cooke-Glenmont, but decreased by 69.7% at Indian Springs (Table 7). Perhaps OP annual load fluctuations are related to hydrology and GI age. Perhaps a longer hydraulic retention time at Indian Springs allows OP to adsorb to clay and silt instead of a fast infiltration rate leaching OP from organic matter. Also, perhaps mineralization more readily occurred at Indian Springs because compost within bioretention media was younger.

PBP annual loads decreased to a similar extent at Cooke-Glenmont and Indian Springs, 59.7 and 66.4%, respectively (Table 7). Slightly higher reductions may have occurred at Indian Springs because permeable pavement covered a substantial percentage of the sewershed. Greater TP annual load reduction occurred at Indian Springs (73.3%) than Cooke-Glenmont (51.9%). Since PBP annual load reductions were similar, TP annual load differences were likely due to OP leaching at Cooke-Glenmont and not Indian Springs. Line et al. (2012) reported a similar 54% TP reduction after the installation of GI. Baseline or pre-GI TP annual loads of 2.62 and 4.19 kg/ha/yr at Cooke-Glenmont and Indian Springs, respectively, were greater than the 1.7 kg/ha/yr reported for a residential area (Line et al., 2002). Meanwhile, post-GI TP annual loads of 1.26 and 1.12 kg/ha/yr were less than that reported for a residential neighborhood without GI.

TSS annual load reductions of 83.8 and 95.3% were observed at Cooke-Glenmont and Indian Springs, respectively (Table 7). These reductions are larger than reported LSM reductions for storm event load reported in section 1.3.5. because annual load reductions were calculated as a simple arithmetic mean. A significant difference existed in 5-minute peak rainfall intensity, with baseline or pre-GI having a higher peak intensity than post-GI. This difference was not accounted for using the simple arithmetic mean, so annual loading percent reductions are likely exaggerated. Other residential and commercial GI studies reported similar annual TSS load reductions of 92-97% (Page et al., 2015, Line et al., 2012), but they treated a larger, upwards of 90%, area of the sewershed. Pre-GI annual TSS loads of 2114 and 5198 kg/ha/yr for Cooke-Glenmont and Indian Springs, respectively, exceeded the 1958 kg/ha/yr annual TSS load reported for a residential neighborhood reported by Line et al (2012). Post-GI annual loads of 343 and 242 kg/ha/yr for Cooke-Glenmont and Indian Springs, respectively were substantially less than the typical TSS annual load for a developed area.

1.4 Summary and Conclusions

This study of GI retrofitted in residential sewersheds greater than 10 ha identities clear water quality benefits. These benefits were realized at relatively low ratios of BRC to sewershed area. While recommendations range from 5-10% (Roy-Poirier et al., 2010b), these ratios were 0.38 and 1.91% for the sewersheds in this study. Retrofitting bioretention into easements, along curbs, and within regional depressions, and exchanging asphalt for permeable pavement are feasible GI activities for municipalities. These GI practices offer a tangible option for municipalities to improve residential stormwater quality. It is recommended that municipalities first consider the maintenance required to maintain GI systems (street sweeping, mulching, etc.). Also, installing an IWS in GI practices may provide municipalities with further water quality improvements. This study has inherent limitations as only 1-2 years of post-GI data have been collected to date. Further monitoring will reveal the long-term implications municipalities can expect from adopting GI on this scale. Conclusions drawn from this study include:

- After the installation of GI, sewersheds had significantly lower concentrations of TAN (60.5-64.0%), TKN (14.1-16.5%), and TN (13.7-24.1%). Storm event loads also significantly decreased for TAN (47.1-67.7%), TKN (19.9-20.9%), and TN (24.0-25.4%). Nitrate concentrations and storm event loads did not significantly change with the implementation of GI. GI treated nitrogen pollutants to the same extent, regardless of a small or large storm event. Nitrogen transformations were more abundant than reductions.

- OP concentrations significantly decreased (25.2%) in one sewershed, but insignificant OP leaching was seen in the another. Infiltration rates and hydrologic retention times likely influence OP uptake, along with sorption and vegetative uptake. PBP concentrations and loads significantly decreased (by 30.9-66.5 and 40.3-49.2%, respectively) due to sedimentation and filtration of particulates. TP concentrations and loads significantly decreased with the adoption of GI (by 20.9-47.4 and 27.8-32.6%, respectively). PBP sedimentation occurred to a greater extent than OP leaching or adsorption. TP reductions were similar regardless of small or large rainfall events.
- TSS concentrations and loads were significantly reduced by 61.6-67.7 and 59.5-78.3% with the adoption of GI. Having fewer GI practices, while treating a larger percentage of the sewershed resulted in greater TSS storm event load reductions. GI was better suited to treat TSS during smaller precipitation events.

Chapter 2. Significant Reductions of Heavy Metals in Residential Stormwater from Sewershed-Scale Green Infrastructure

2.0 Abstract

Buildings, automobiles, and roads are major sources of heavy metals in urban areas. Stormwater runoff pushes sediment-bound and dissolved heavy metals to aquatic ecosystems. Green infrastructure (GI) is a novel way to address the runoff of pollutants to improve water quality. Examples of GI include bioretention and permeable pavement. Using soil and plants as natural filters, these solutions have been shown to reduce heavy metals, but never across entire sewersheds at scales above 10-ha. The Blueprint Columbus project is a large-scale implementation of GI with goals of absorbing and filtering stormwater runoff. The goal of this research is to address this gap in knowledge by evaluating reductions of heavy metals in stormwater runoff from the Blueprint Columbus projects that installed GI across entire sewersheds. The objectives of this study are to quantify sediment and heavy metals (Cd, Cr, Cu, Ni, Pb, and Zn herein) changes at 11.5 and 47.8 ha sewersheds as a result of GI and analyze causation for these changes. Water quality samples were collected over three and a half years at the discharge point of one control and two treatments sewersheds located in the Clintonville neighborhood of Columbus, Ohio. A network of various technologies, including tipping rain gauges, area-velocity meters, and ISCO water samplers were utilized to continuously collect water quality data. The experimental technique, known as a before-after, control-impact (BACI) paired sewershed approach, resulted in a robust comparison of pollutant concentrations and loads before and after the installation of GI. Significant load

reductions with the installation of GI were observed for all heavy metals analyzed herein, and event mean concentrations significantly reduced for Cu. Cd, Cu, Pb, and Zn event mean concentration reductions were 64.3-69.9, 35.1-37.0, 48.7-58.3, and 25.2-45.5%, respectively. Percent load reduction trends were Cd>Pb>Cu>Zn>Ni>Cr. Land use and GI density had substantial impacts on heavy metal presence and reduction, respectively. This study provides evidence of heavy metal reductions occurring on a sewershed scale for a GI project. In turn, GI projects of this scale offer an opportunity for improved water quality, influencing municipalities, aquatic ecosystems, and public health.

2.1. Introduction

Plants and animals require trace amounts of heavy metals, including chromium(III), copper and zinc, for metabolic processes; however, exposure beyond trace amounts can be toxic (Singh et al., 2011; Willey & Zvalaren, 2002). Further, other heavy metals, such as cadmium, chromium(VI), and lead bioaccumulate in tissues and may cause acute or chronic toxicity, depending on concentration (Davidson et al., 2004; Malik et al., 2010). This toxicity threatens human health and aquatic ecosystems (Baby et al., 2011; Ma et al., 2016; Tchounwou et al., 2012). In an attempt to limit the presence of heavy metals in air, soil, drinking water, and aquatic ecosystems, maximum contaminant levels have been developed (Duruibe et al., 2007). The U.S. EPA's acute ambient water quality criteria for aquatic life are 1.8, 570, 16, 4.7, 470, 82, and 120 µg/L for Cd, Cr(III), Cr(VI), Cu, Ni, Pb, and Zn, respectively (USEPA 2003; Le Fevre et al., 2015).

Heavy metals are the main cause of ecotoxicity and have resulted in numerous public health crises (Brudler et al., 2019; Matsuo, 2003). These range from the 20th century, Hg-induced Minamata disease in Japan (Funabashi, 2006) to the 2014 Pb-induced drinking water disaster in Flint, Michigan (Hanna-Attisha et al., 2016). Urban stormwater runoff poses a critical threat to human health due to the presence of multiple heavy metals within (Gaffield et al., 2003; Ma et al., 2016). Heavy metals, among other toxins, in urban stormwater runoff have caused salmon mortality, and these heavy metal toxins are also present within supermarket fish (Burger & Gochfeld, 2005; McIntyre et al., 2018). Heavy metal toxins from urban areas in fish and vegetables present major health risks, especially for children (X. Wang et al., 2005).

The presence of heavy metals in stormwater runoff is a product of materials utilized to construct the urban environment, and some heavy metals are transported in stormwater runoff regardless of the land use type (Göbel et al., 2007). Sources of heavy metals in urban areas include industrial processes, buildings and roofs, galvanized metals, automobile coatings, brake pads, tires, and roadways (Brown & Peake, 2006; Davis et al., 2001; Ellis et al., 1987), and natural sources such as rocks and dust. Cd is associated with automobile brakes, welding, and batteries (McKenzie et al., 2009; Singh et al., 2011). Sources of Cr in urban areas are both natural, such as the weathering of rocks, and anthropogenic, including the corrosion of metal plates, dyes and paints, and fossil fuel combustion (Makepeace, Smith, & Stanley, 1995; Willey & Zvalaren, 2002). Sources of Cu in urban areas include road debris, metal piping, and automobiles (Brown & Peake, 2006; McKenzie et al., 2009; Singh et al., 2011). Roofs, paints, and brakes are major sources of Pb in urban areas (Müller et al., 2020). Tires and car ignitions are anthropogenic sources of Ni in urban areas, and organics, vegetation, and dust are common natural sources (Aryal et al., 2010; Makepeace et al., 1995). Sources of Zn in urban areas include galvanized roofs, gutters, plumbing, and automobile traffic (Brown & Peake, 2006; Müller et al., 2020; Singh et al., 2011).

These heavy metals exist in dissolved, colloidal, and particulate forms (Guéguen & Dominik, 2003). In urban stormwater runoff, Pb and Cr are highly particulate bound, Ni is related to particles and organic matter, Zn can adsorb to sediment and colloids but is mostly associated with dissolved solids, and Cd and Cu are largely related to dissolved solids and colloidal materials (Makepeace et al., 1995; Maniquiz-Redillas & Kim, 2016). Birch and Rochford (2010) found that heavy metals in stormwater are primarily particulate bound, ranking their affinity for particulate form as: Pb>Zn>Cu>Cr>Cd>Ni. In urban areas, street runoff demonstrated the highest percentage of heavy metals, Cd, Cu, Pb, and Zn in the particulate form (72-97%), followed by yard (71-95%) and roof runoff (9-87%; Gromaire-Mertz et al., 1999). Since heavy metals are highly particulate-bound, it has been suggested that indirect metal pollutant load can be deduced from total suspended solids (TSS) measurements in some cases (Hallberg et al., 2007).

Humans encounter heavy metals from stormwater by consuming tainted surface, groundwater (Muhammad et al., 2011), and fish (Alrabie et al., 2019), and through physical contact with surface water and stormwater runoff (Gunawardena et al., 2013; Müller et al., 2020; Stead-Dexter & Ward, 2004). Low impact development (LID; Ahiablame et al., 2012; Dietz, 2007) is a land development strategy that mitigates negative impacts of heavy metals from stormwater by employing stormwater control measures (SCM). Green infrastructure (GI) is a promising SCM method to reduce human exposure to heavy metals from stormwater. This technology mitigates heavy metal loads to surface waters by attenuating and passively treating stormwater runoff. GI technologies, including bioretention and permeable pavement, have been shown to sequester heavy metals from stormwater prior to discharge to surface waters (Davis et al., 2003; Scholz & Grabowiecki, 2007). This sequestration has been designed for filtration of particulate matter to which heavy metals are preferentially adsorbed, adsorption to soil media, and microbial and vegetative uptake (Bean et al., 2007; Lijklema, 1980; Muerdter et al., 2018; Muthanna et al., 2007; J. Wang et al., 2017).

Many laboratory studies and analyses of single or small clusters of bioretention have demonstrated substantial heavy metal reductions. Bioretention reduces heavy metal concentrations by orders of magnitude (Trowsdale & Simcock, 2011). Laboratory bioretention studies demonstrated Cu, Cd, Pb, and Zn reductions in the range of 72 to nearly 100%, where soil captured 88-97% of these heavy metals and another 0.5-7% accumulated in plants (Davis et al., 2003; Muthanna et al., 2007; Sun & Davis, 2007). A field study of two bioretention systems draining 0.28-0.45 ha asphalt parking lots in Maryland demonstrated median event mean concentration (EMC) reductions for Cr, Cu, Pb, and Zn of 0-8, 0-31, 0-55, and 55-80%, respectively. Similarly, load reductions were 60-100, 65-96, 83-100, and 92-99%, (Li & Davis, 2009). The International Stormwater BMP database, which provides up to 520 bioretention performance data points from field studies, reported significant reductions from the influent to effluent of individual bioretention cells for Cr, Cu, Pb, and Zn total concentrations (21.9, 38.0, 89.9, and 75.9%

reductions, respectively), but not Cd and Ni (Clary & Jones, 2016). Heavy metal removal occurs preferentially at the surface of the bioretention cell, where filtration, capture, and degradation take place in the surface mulch layer; filtration, microbial activity, ion exchange, adsorption, and vegetative uptake occur in the subsequent planting layer (Davis et al., 2009; OEPA, 2006). Jones and Davis (2013) found that the majority of metal accumulation within bioretention occurs near the inlet of the practice and in the top 3-12 cm of the soil media. The high cation exchange capacity and organic matter content of bioretention media result in capture of dissolved heavy metals while filtration at the surface removes the vast majority of particulate bound heavy metals (Robertson et al., 1982; Sun & Davis, 2007).

Other studies have demonstrated significant particulate and heavy metal removal from permeable pavement alone. Permeable pavement efficiently traps sediment and heavy metals in surface runoff (Scholz & Grabowiecki, 2007), which is the reason that these systems clog over time (Winston et al., 2016). Past studies demonstrated the concentration of Cu, Pb, and Zn in permeable pavement exfiltrate was significantly lower than from typical asphalt runoff (Bean et al., 2007; Brattebo & Booth, 2003; Drake et al., 2014). Another showed 59, 84, 77, and 73% load reductions for TSS, Pb, Cd, and Zn, respectively, provided by porous asphalt (Legret & Colandini, 1999). The International Stormwater BMP Database reported significant reductions in total concentration from the influent to effluent of permeable pavement for Cu, Ni, Pb, and Zn (35.8, 83.0, 52.4, and 75.6% reductions, respectively), but not Cd and Cr (Clary & Jones, 2016).

A network of GI retrofitted into a residential neighborhood has also shown promise for heavy metal reductions. A 0.53-ha residential sewershed in North Carolina retrofitted with a bioretention cell, four permeable pavement parking spaces, and a tree filter demonstrated significant Cu, Pb, and Zn EMC reductions of 82, 62, and 89%, respectively; loading reductions were significant and substantial: 54, 88, and 77%, respectively (Page et al., 2015). Meanwhile, a 1.7-ha sewershed in Connecticut equipped with twelve bioretention cells and permeable interlocking concrete pavers demonstrated a non-significant 25% reduction in Cu EMC, 67% reduction of Pb EMC, and 77% reductions of Zn EMC (Bedan & Clausen, 2009). Annual loads of Cu, Pb, and Zn decreased 50, 79, and 81%, respectively.

Although other studies have shown the success of GI practices in removing heavy metals at the site scale and at the small subcatchment scale (<2 ha), none have quantified concentration and load reductions at a neighborhood scale larger than 10 ha. While these previous studies have measured how GI impacts heavy metal transport, understanding how differing size and density of GI retrofitted into adjacent sewersheds impacts heavy metals is an important gap in knowledge. Addressing these unknowns will provide guidance to municipalities that are adopting GI practices at greater spatial scales, which in turn benefits public health and aquatic ecosystems. The research objectives of this sewershed-scale residential GI study address this knowledge gap by 1) using a before-after, control-impact paired watershed approach to quantify changes in heavy metals resulting from the implementation of GI on a sewershed scale, 2) discussing fundamental processes responsible for these water quality changes, 3) evaluating if GI is better suited for water quality treatment for smaller or larger storm events, and 4) comparing annual pollutant load reductions in two adjacent sewersheds with varying GI density and storage.

2.2 Materials and Methods

2.2.1 Site Description

Three sewersheds in the Clintonville neighborhood of Columbus, Ohio were monitored for stormwater flow and heavy metals at their respective outfalls (Figure 5). The sewersheds were 3.6-17.4% commercial and institutional land use. The study region is single-lot, residential family plots constructed between 1910 and 1950. Soils in the neighborhood were mapped as silt loam in the Cardington and Bennington soil series (Table 1; NRCS Web Soil Survey, 2019). This region experiences four distinct seasons, with winter temperatures in the range of -6 to 3°C, and summer temperatures in the range of 18 to 29°C. Long-term average annual precipitation is 1,000 mm, including an average of 70 mm of snowfall (NOAA 2020).

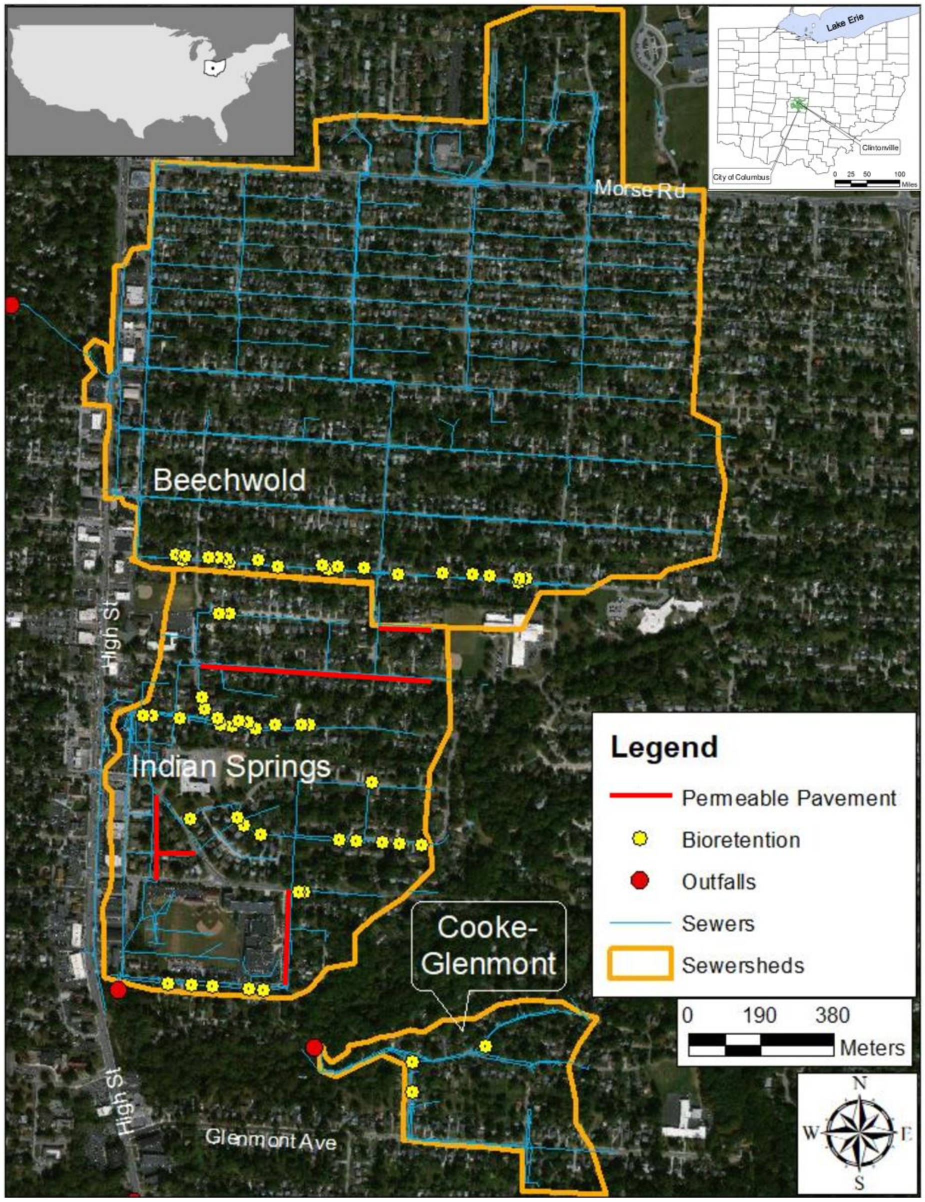

Figure 5: Map of sewersheds. Control (Beechwold) and treatment (Indian Springs and Cooke-Glenmont) sewersheds are outlined in orange. Blue lines indicate storm sewers. Red lines represent permeable pavement. Yellow dots represent bioretention cells, and red dots indicate storm sewer outfalls where sample collection occurred.

Table 8: Sewershed Characteristics

Sewershed	Area (ha)	Land Use (%)			Imperviousness (% of Total Area)	GI Surface Area (% of Sewershed Area)	% Sewershed Area Draining to Bioretention	Sewershed Storage Added by Bioretention* (mm)
		Residential	Commercial	Institutional				
Beechwold	111.5	95.7	3.6	0.7	38.2	0.0074	2.1	0.0075
Indian Springs	47.8	75	7.6	17.4	40.3	1.91	23.6	0.19
Cooke-Glenmont	11.5	100	0	0	30.9	0.38	30.1	1.63

*Land surveying was used to measure added sewershed storage from bioretention and permeable pavement in late 2019 through early 2020. Accumulated mulch and detritus since construction ended to when land surveying occurred may have occupied some of the bioretention bowl storage

The control and treatment sewersheds were located within a 1 km radius. Since the majority of the 111.5-ha Beechwold sewershed was not retrofitted (only 0.0074% of the sewershed was covered by GI on a single street), it served as the control for the experiment (Table 8). This sparse GI at Beechwold was installed the same timeline as GI at Indian Springs. Statistical testing to show this GI did not affect heavy metals at Beechwold, but rather sewershed and rainfall characteristics, will be presented in section 2.3.1; therefore, Beechwold is appropriate for use as a control.

Residential land use ranged from 75-100% among the sewersheds, with interspersed commercial land uses along major thoroughfares and institutional (i.e., schools) land uses. Imperviousness ranged from 30.9% at Cooke-Glenmont, which was located in a forested area near a ravine, to 40.3% at Indian Springs. Indian Springs had the highest percentage of institutional land use (17.4%) which contributed substantial directly connected impervious areas (i.e., large roofs and parking lots). The three largest sources of imperviousness in the sewersheds were roofs (12.5-15.7%), roads (8.6-11.0%), and driveways (6.4-8.3%), respectively.

Different types and densities of GI were retrofitted into the Indian Springs and Cooke-Glenmont sewersheds. Thirty-two bioretention cells and five permeable pavement roads or alleys were constructed in the 47.8-ha Indian Springs sewershed over approximately a 1-year period. GI practices covered 1.91% of the sewershed surface area, and bioretention treated 23.6% of the sewershed area, adding 0.19 watershed millimeters of storage in the sewershed (Table 8). Cooke-Glenmont, the smallest sewershed at 11.5 ha, had two regional bioretention cells and a third cell retrofitted within its boundaries.

Taken together, this GI accounted for 0.38% of the sewershed area and treated 30.1% of its surface area. These three cells added 1.63 sewershed mm of storage.

2.2.2 GI Retrofits

Among the 32 bioretention cells at Indian Springs, 11 protruded into the street to intercept runoff along the curbline (Figure 6a). The other 21 were located behind the curb in the easement in front of houses (Figure 6b). All bioretention cells in this area were equipped with an underdrain, with a media depth of approximately 60 cm above the underdrain. The median bioretention cell surface area at Indian Springs was 8.74 m^2, treating a median drainage area of 0.26 ha. There was no internal water storage (i.e., an upturned elbow in the underdrain providing storage for inter-event exfiltration) for bioretention in this sewershed. Bioretention cells were planted with (1) grasses, especially *alamagrostis acutiflora*, *panicum virgatum*, and *pennisetum alopecuroides* (2) perennials including *asclepias tuberosa*, *iris versicolor,* and *rudbeckia fulgida*, and (3) shrubs such as *hypericum frondosum*. Indian Springs was the only sewershed where permeable pavement was installed (Figure 5; Figure 6c). Five roads or alleys were retrofitted with curb-to-curb permeable pavement with a total surface area of 8,742 m^2, representing 1.83% of the sewershed area. The typical cross section was 65-150 cm deep and given the low hydraulic conductivity of the soils in the neighborhood, an underdrain was also employed in all five permeable pavements.

At Cooke-Glenmont, regional bioretention cells were installed in series. The upstream cell had a surface area of 152.1 m^2 occupying 0.13% and treating 15.8% of the sewershed (Figure 6d). A second, larger (255.4 m^2) bioretention cell was located downstream, and treated effluent from the upstream cell (Figure 6e). It occupied 0.22% and treated a total of 24.4% of the sewershed. The smallest (28.1m^2) bioretention cell at Cooke-Glenmont occupied 0.02% and treated 5.4% of the sewershed (Figure 6f). Characteristics of the bioretention cell included 60 cm of bioretention media, 30 cm of drainage aggregate surrounding an underdrain, and 30 cm of bowl storage. Internal water storage was not employed in bioretention cells in Cooke-Glenmont. Regional bioretention cells were planted with (1) grasses and sedges, such as *panicum virgatum* and *carex morrowii*, and (2) perennials, especially *polygonatum odoratum*, *rudbeckia fulgida*, and *symphyotrichum ericoides*, Bioretention in both treatment sewersheds utilized the same media which met the state standards as defined by OEPA (2006).

Figure 6a-f: Green infrastructure practices. Bioretention (a-b) and permeable pavement (c) utilized in the Indian Springs Sewershed. Bioretention (d-f) utilized in the Cooke-Glenmont sewershed

2.2.3 Construction and Monitoring Timeline

GI construction occurred independently and on different timelines at the treatment sites (Table 9). Broadly, monitoring was divided into three phases: 1) pre-GI 2) construction and 3) post-GI. The pre-GI phase refers to the period before the construction of GI. The construction phase refers to the period during GI construction; data from this phase were not analyzed for Indian Springs, since the goal of this work was to assess pre- and post-GI differences in water quality. Post-GI refers to the period when GI facilities were brought online. Some secondary project construction (i.e., redirecting downspouts, implementing sump pumps, and lining sanitary sewer laterals) occurred at Indian Springs during the post-GI phase.

In the case of Cooke-Glenmont, pre-GI and construction phases were combined to form the “baseline” phase. The first water quality sample at Cooke-Glenmont was not collected until September 29, 2016 and the last sample before construction commenced was collected on December 6, 2016. Combining these project phases augmented the roughly two months of pre-GI data with 7.5 months of additional data, allowing for improved comparisons of changes in water quality pre- and post-GI retrofit. This larger baseline data set also allows the impacts of seasonal changes to water quality to be captured. The combination of these project phases was further justified using the Kruskal-Wallis test as presented in section 2.3.1.

During winter months, sampling equipment was removed to avoid damage to it from ice and snow. Equipment was not deployed during the following periods:

December 19, 2016 to March 19, 2017, December 6, 2017 to March 2018, and December 6, 2017 to March 20, 2018 (Table 2).

Table 9: Construction and Monitoring Timeline

	Project Phase	
Sewershed	Pre-GI/Baseline	Post-GI
Cooke-Glenmont*	9/29/2016-7/13/2017	9/14/2017-8/13/2019
Indian Springs**	9/30/2016-11/19/2017	10/29/2018-8/26/2019
	Monitoring Period	
Control	9/29/2016	12/9/2019

*Baseline phase at Cooke-Glenmont includes construction phase
**Secondary construction projects were happening at Indian Springs during post-GI

2.2.4 Experimental Design and Data Collection

This study utilized a before-after, control impact (BACI) design to determine if heavy metal changes in stormwater were due to GI or other external factors, such as changes in climate or pollutant generation in the sewersheds (Green, 1993; Page et al., 2015; Shuster & Rhea, 2013). Water quality samples were collected before and after GI was installed at both control (Beechwold) and treatment sewershed (Indian Springs or Cooke-Glenmont) outfalls.

A 0.254-mm resolution tipping bucket (Davis Rain Collector) and a manual rain gage were deployed within or adjacent to the control and both treatment sewersheds. They were attached to a 180-cm tall wooden post in locations free from overhead obstructions. Rainfall data from the tipping bucket rain gages were stored on Hobo

Pendant data loggers (Onset Computer Corporation, Bourne, Massachusetts). Rainfall data were stored on a 1-minute interval. Readings were verified and automated sampler pacing was re-calibrated after each using manual rain gage measurements, as described below.

The Cooke-Glenmont outfall was ephemeral, while Indian Springs and Beechwold had continuous baseflow. Cooke-Glenmont and Beechwold were equipped with an area velocity meter (AVM; Teledyne Isco, Lincoln, Nebraska), which communicated with ISCO 750 module attached to an ISCO 6712 sampler. Meanwhile at Indian Springs, AVMs transmitted measurements to an ISCO 2150 flow module and data were stored on an ISCO 2100 sample interface module. These modules communicated with an ISCO 3700 series sampler. Collectively, flow modules determined flow rate on 1-minute intervals. Flow rate was integrated with time to determine runoff volume and to trigger sample aliquots obtained by automated samplers.

All composite samples were composed of a minimum of five and a maximum of 50, 200 mL aliquots describing greater than 80% of the pollutograph (U.S. EPA 2002). Composite samples were vigorously shaken within 18.9L bottles to ensure suspension of particulate matter and a well-mixed, EMC. Aliquots were paced such that up to a 50-mm event could be sampled.

In a few cases (i.e., two times at Beechwold and once at Cooke-Glenmont), two composite water quality samples were obtained during a single storm event due to rainfall depth exceeding the 50-mm maximum depth When this occurred, a runoff volume weighted average concentration was used in the analysis. Because of the short antecedent dry period (six hours) used to separate rainfall events, one to three samples at each site represented the water quality of multiple hydrologic events. This occurred when the flow had not returned to baseflow before the onset of the next rainfall event, causing the samplers to combine two storms within the composite bottle. In these cases, the separate hydrologic events were combined for pollutant concentration and load analysis.

2.2.5 Data Analysis

Since heavy metals have been shown to be largely sediment-bound in urban stormwater runoff (Birch & Rochford, 2010; Gromaire-Mertz et al., 1999; Hallberg et al., 2007), TSS results are presented herein. Summary statistics for TSS and heavy metal concentrations and storm event loads were determined using laboratory-reported EMCs. These included the number of observed events, median pollutant concentrations, and pollutant loads during each phase (i.e., baseline, pre-GI, or post-GI) for control and treatment sewersheds. Observed changes in water quality due to GI implementation were compared to other similar studies. They were also compared to influent and effluent summary statistics and EMCs for individual GI practices from the International Stormwater BMP Database (Clary & Jones, 2016).

Storm event heavy metal loads from each sewershed were determined as the product of pollutant EMC and runoff volume on a storm-by-storm basis. TSS and heavy metal loads were reported on a sewershed area-normalized basis and were calculated using the following equation:

$$L_{\mathrm{i}} = 1 \times 10^{-3} \times \frac{EMC_{\mathrm{i}} \times V}{A_{WS}} \quad (1)$$

where L_i is the load of pollutant i (g/ha), EMC is the event mean concentration (mg/L), V is the runoff volume (L) measured after discounting baseflow, A_{WS} is the sewershed area (ha), and the constant converts from milligrams to grams.

Annual loading (L_m, kg/ha/month) was estimated by accounting for storms not sampled for water quality. The ratio of long-term average annual rainfall depth (RF_{LTA}; mm/yr) to total rainfall depth sampled for water quality (RF_{SAMP}; mm) was utilized to scale the annual loading (Equation 2). Thus, we assume that the sampled storm events are representative of the overall population of runoff volume and pollutant concentration. The annual loading was also normalized by sewershed area and monitoring period duration (d_{MP}, years):

$$L_a = 1 \times 10^{-3} \times \frac{\sum_{i=1}^{n}(EMC_i \times V_i) \times RF_{LTA}}{A_{WS} \times RF_{SAMP}} \quad (2)$$

where n is the number of sampled storm events. To determine the effects of different event depths on annual load, bins of event depth were created and the load within each bin was summed. This load was then scaled by the ratio of the total rainfall depth to the total sampled rainfall depth within each bin to estimate the total load by event depth bin. Annual loading was calculated by considering each project phase to be an individual monitoring period. Since water quality samples were not collected during the cold winter months, annual loading presented herein extrapolates for these months.

Among the three monitored sewersheds, comparisons between sampled and observed rainfall events, rainfall characteristics, pollutant concentration, and pollutant load were made to determine significant differences. The Wilcoxon rank sum test was used to determine if sampled storm event characteristics varied from those of all observed storms. Using the Kruskal-Wallis test, rainfall characteristic comparisons were made across sewersheds and across project phases. TSS and heavy metal data were log transformed, after which the Shapiro-Wilk test was used to check for normality of model residuals. When a linear relationship was present in the data, model residuals were normally distributed, demonstrated homoscedasticity, and showed no multicollinearity, analysis of covariance (ANCOVA) was used to compare treatment to control data. ANCOVA analysis was utilized to uncover significant differences in the slopes and intercepts of TSS and heavy metal concentration and storm event load parameters (Page et al., 2015). If the residuals were not normally distributed, yet the sample size was large (>30), parametric statistical analysis methods were still used (Ghasemi & Zahediasl, 2012) since sample sizes were large enough to approximate the population. When a significant linear relationship did not exist for water quality parameters during the pre-GI phase, but was present for the post-GI phase, a paired t-test was used to compare control and treatment sewersheds during the post-GI phase. No statistical analyses were performed on TSS or heavy metal data lacking either an adequate sample size or a significant linear relationship. Percent changes in pollutant concentration and storm event load were calculated and reported using least squares mean (LSM) analysis:

$$Change\ (\%) = \left(\frac{10^{\bar{Y}_{Post}}}{10^{\bar{Y}_{Pre}}} - 1\right) \times 100 \qquad (3)$$

where $\bar{Y}_{Post}$ is the treatment sewershed LSM during the post-GI phase, and $\bar{Y}_{Pre}$ is the treatment sewershed LSM during the pre-GI phase. Herein, percent concentration and storm event load percent differences observed after the adoption of GI refer to the LSM percent difference. On the other hand, the percent difference between annual load by project phase is simply reported as percent change (since annual load is a single value, not a distribution that can be statistically tested). All stormwater data analysis was completed using R statistical software version 3.4.2 (R Core Team 2018). Except where noted, a criterion of 95% confidence (α=0.05) was used.

2.2.6 Laboratory Techniques

After fully suspending particulate pollutants, composited samples were divided among a 500 mL pre-acidified bottle for Cd, Cr, Cu, Ni, Pb, and Zn analysis and a 500 mL for TSS analysis. Samples were collected within 24 hours after the cessation of rainfall, placed on ice (<4ºC), and transported to the laboratory. Samples were analyzed using either U.S. EPA (1983) or American Public Health Association (APHA et al. 2012) methods. A value of one-half the detection limit was substituted for EMCs below the method detection limit (MDL; Antweiler and Taylor 2008; Table 10). Analytes exhibiting a moderate amount of below detection limit (BDL) concentrations (i.e., 10-35% of sampled events) were: TSS at all three sewersheds (Beechwold 15.2% BDL; Cooke-Glenmont 10.8% BDL; Indian Springs 25.0% BDL), and Cd at Beechwold (14.1% BDL) and Indian Springs (24.3% BDL). For all other analytes, BDL concentrations were observed for fewer than 10% of sampled storm events. All concentrations above MDL were analyzed without transformation.

Table 10: Laboratory methods, preservation procedures, and method detection limit (MDL) for sediment and heavy metals

Parameter	Abbreviation	Laboratory Method	Preservation	MDL (μg/L)
Total Suspended Solids	TSS	Standard Methods 2540D2	<4˚C	2000
Cadmium	Cd	EPA 200.8	HNO_3 (<2 pH), <4˚C	0.013
Chromium	Cr			0.036
Copper	Cu			0.26
Nickel	Ni			0.025
Lead	Pb			0.0086
Zinc	Zn			0.7

2.3 Results and Discussion

2.3.1 Justification of Experimental Setup

Following the same timelines as Cooke-Glenmont for baseline and post-GI, and pre- and post-GI at Indian Springs, significant difference in Cd, Cu, and Zn concentration were observed at Beechwold ($p<0.05$). Further, TSS concentrations exhibited a significance difference at Beechwold following the project timeline for Indian Springs ($p<0.05$). These heavy metals have been shown to be 72-94% and 72-80% particle bound in urban stormwater runoff from yards and streets, respectively (Gromaire-Mertz et al., 1999). For this reason, these heavy metal differences were assumed to be related to TSS. In all these cases, baseline or pre-GI concentrations were greater than post-GI. During the time frames corresponding with pre- and post-GI phases at Indian Springs, median 5-minute peak rainfall intensities for sampled events at Beechwold were 22.1 and 13.0 mm/hr, respectively. Past studies have shown high rainfall intensities to drive TSS due to sediment erosion (Sharma et al., 2016). Since GI installed at Beechwold only treated 2.1% of the sewershed surface area and no other water quality parameters exhibited significant differences with project phase, Beechwold was used for the control.

Combining the pre-GI and construction phases at Cooke-Glenmont to create the baseline phase increased the data set from roughly two to 9.5 months (n = 7 to 25 storms), which resulted in a more robust dataset to compare with post-GI. No pollutants exhibited a significant difference in pollutant concentrations between the pre-GI and construction phases. Elevated TSS and heavy metal concentrations have been shown to be elevated during construction (Alsharif, 2010; Atasoy et al., 2006; Müller et al., 2020).

Since no significant difference in concentration was observed between pre-GI and construction project phases, those phases were combined at Cooke-Glenmont and called "baseline."

2.3.2 Characteristics of Sampled Events

At Beechwold, Cooke-Glenmont, and Indian Springs, 102, 67, and 40 storm events, respectively, were sampled for water quality during the monitoring period or project phases as described in Table 1. During these periods, storm events sampled for water quality represented 39.1-67.5% of the total rainfall. The median event depth for sampled storms ranged from 14-16.8 mm across the sewersheds, slightly greater than the median event depth for observed storms of 9.7-10.4 mm. This can be attributed to minimum sample volumes required for laboratory analyses, which precluded the analysis of storms less than 3 mm. The median 5-minute peak rainfall intensity for sampled storms, which ranged between 13.7 and 18.3 mm/hr across the sewersheds, was similar to the median peak intensity recorded for all observed storms (13.7-15.2 mm/hr). The median ADP for sampled events (2.7-3.7 days) was similar to the median ADPs determined from all observed events in the sewersheds (3.1-3.3 days).

The Wilcoxon rank sum test showed a significant difference existed between observed and sampled storms for rainfall depth ($p<0.001$), but no significant differences existed for other rainfall characteristics (i.e. average intensity, peak 5-minute intensity, ADP, and rainfall duration). From these results, we can conclude that the sampled storm events were representative of the overall distribution of storms observed in the sewersheds during the monitoring period. Furthermore, no significant difference in the previously mentioned rainfall characteristics existed between pre- and post-GI phases at Indian Springs, and between baseline and post-GI phases at Cooke-Glenmont, except for 5-minute peak rainfall intensity ($p<0.05$). Generally, median 5-minute peak intensities during the baseline or pre-GI phase (16.8-22.9 mm/hr) were greater than the post-GI phase (10.7-13.7 mm/hr) for sampled events.

Results from Kruskal-Wallis k-sample tests showed that rainfall characteristics did not significantly differ between the three sewersheds (p>0.68 in all cases; Kruskal & Wallis, 1952). This is logical as the sewersheds are within 1 km of each other.

2.3.3 Total Suspended Solids

Since heavy metals are largely particulate bound, TSS discussion is included herein. TSS concentrations decreased by 61.6%, from 160 to 49 mg/L, at Cooke-Glenmont with the installation of GI ($p<0.001$; Table 11). A 78.3% reduction in TSS storm event load was observed at Cooke-Glenmont. ANCOVA analysis for this sewershed revealed that the difference in intercepts were not significant ($p>0.5$), but slopes were significantly different between the baseline and post-GI periods for TSS storm event loads ($p<0.005$; Figure 7). This implies that bioretention at Cooke-Glenmont may be better suited for reducing TSS storm event loads for smaller storm events. TSS concentration decreased 61.6% between the pre- and post-GI phases at Indian Springs, with median concentrations changing from 83 to 20 mg/L, and TSS storm event load decreasing by 59.5% with the installation of GI (Table 5). Median TSS concentrations during the post-GI phase at both treatment sites (49 and 20 mg/L for Cooke-Glenmont and Indian Springs, respectively), were larger than those reported by the International Stormwater BMP Database for effluent from single bioretention cells and permeable pavement (10.0 and 26.0, respectively; Clary & Jones, 2016). This implies further TSS reduction is possible through GI. While a reduction in TSS concentration was observed at Beechwold during the time frame corresponding to pre- and post-GI phases at Indian Springs ($p<0.05$; due to a significant difference in peak 5-minute as described in sections 2.3.1 and 2.3.2), the LSM percent difference accounts for it. For this reason, substantial reductions in TSS concentrations and storm event loading were observed at Indian Springs beyond the reductions observed at Beechwold. Since 30.1% and 23.6% of Cooke-Glenmont and Indian Springs, respectively, were treated by bioretention, yet 61.6-67.7% TSS concentrations reductions were observed, this implies excellent TSS removal. Sedimentation and sediment retention within bioretention cells have shown to effectively decrease TSS concentrations, at times by several orders of magnitude (Trowsdale & Simcock, 2011). In addition to the bioretention, permeable pavement at Indian Springs likely contributed to the decrease in TSS concentration through sedimentation and filtration (Brown et al., 2009). Other residential and commercial GI studies reported significant differences in TSS concentration; Page et al (2015) reported an 82% decrease from 54 to 7 mg/L by treating 91% of a 0.53 ha residential sewershed with an in-street bioretention cell, four permeable pavement parking stalls, and a tree filter. Line et al. (2012) reported a 99% decrease from 65 to 19 mg/L from treating a 7.1 ha LID commercial site with eight bioretention cells, pervious concrete, and a wetland.

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Table 11 Summary statistics for concentrations and storm event loads of total suspended solids (TSS) by project phase at Cooke-Glenmont (CG) and Indian Springs (IS). Interpretations related to project phase were made using an ANCOVA.

	Site	Baseline or Pre-GI Phase			Post-GI Phase			Statistical Results			
		n	Control Median	Treatment Median	n	Control Median	Treatment Median	LSM % Difference	t-value	p-value	Interpretation
Concentration (mg/L)	CG	19	74	160	46	49	49	-61.6	4.2	8.59E-05	Baseline > Post-GI*
	IS	18	51	83	18	30	20	-67.7	-	-	-
Load (kg/ha)	CG	14	3.23	6.47	46	1.69	1.68	-78.3	-0.09	0.926	NSD btw. Phase*
	IS	15	2.07	3.74	16	1.33	1.43	-59.5	-	-	-

Note: NSD implies no significant difference, while dash (-) indicates that statistical analyses were not performed due to insufficient sample size or data failing to meet model assumptions. * indicates a significant difference was observed in ANCOVA slopes, whereas the p-value indicates a significant difference in ANCOVA intercepts, negative LSM % differences imply reduction.

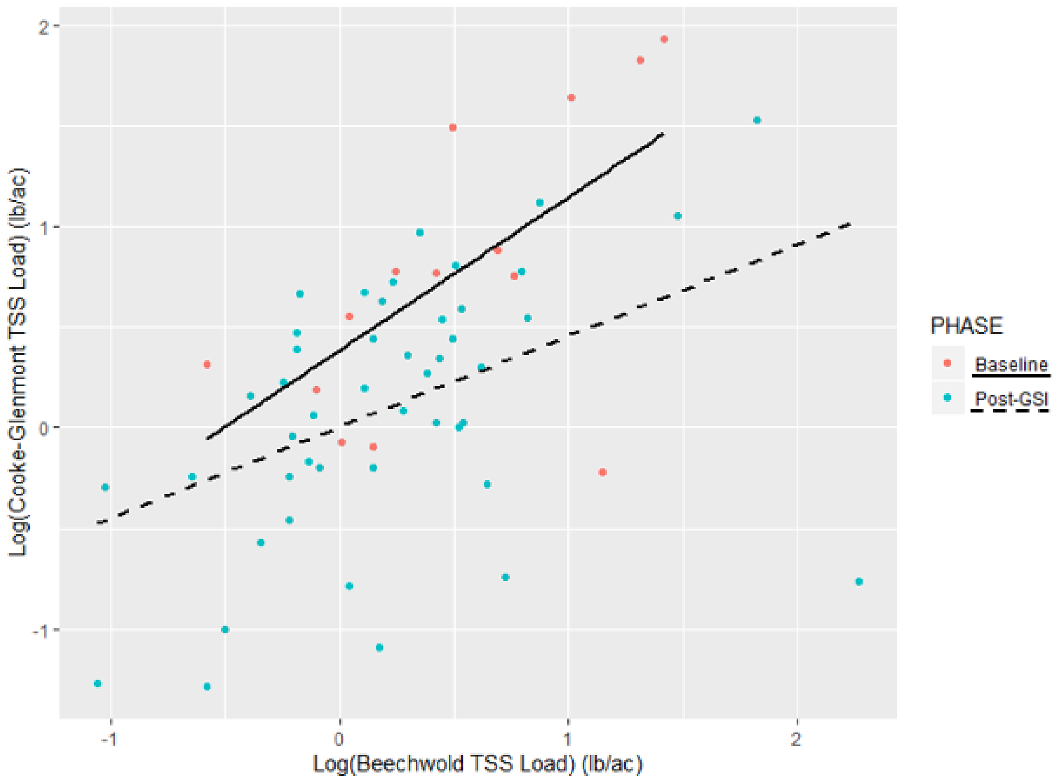

Figure 7: Total Suspended Solids (TSS) loading for Cooke-Glenmont versus control. A significant difference existed in the slopes (p<0.005), but not the intercepts (p>0.5). This indicates bioretention at Cooke-Glenmont is better suited for reducing TSS loading from smaller precipitation events

2.3.4. Heavy Metals

2.3.4.1 Cadmium

No significant difference existed between Cd EMCs at the treatment and control sites during the post-GI phase ($p>0.5$; Table 12). Comparing pre- and post-GI, nonsignificant reductions in Cd concentrations of 64.3 and 69.6% were observed at Cooke-Glenmont and Indian Springs, respectively. These reductions were non-significant because similar reductions were observed at the control site. Median Cd concentrations during the post-GI phase of 0.079 and 0.041 µg/L for Cooke-Glenmont and Indian Springs, respectively, were similar to the 0.07 µg/L reported by the International Stormwater BMP Database for bioretention effluent from a single cell (Clary & Jones, 2016), thus perhaps approaching an irreducible concentration. Similar to sites monitored herein, the International Stormwater BMP Database reported non-significant reductions in total Cd concentrations from influent to effluent for both individual bioretention cells and permeable pavement. Among all heavy metals, median Cd concentrations were most similar to the detection limit of 0.013 µg/L, where 24.3% of samples were below the detection limit at Indian Springs. Perhaps this is due to the residential land use of the sewersheds, where major sources of cadmium would be limited except at intersections where brake wear occurs (McKenzie et al., 2009; Singh et al., 2011).

While concentrations differences were not significant, load reductions of Cd at each treatment sewershed were significantly different: A Cd load reduction of 68.9% occurred at Cooke-Glenmont with the installation of GI ($p<0.001$) and 63.3% at Indian Springs (non-significant; Table 12). At both treatment sewersheds, Cd concentrations and loads exhibited the highest percent removal efficiency of all heavy metals examined herein. A laboratory bioretention evaluation also reported Cd exhibiting the highest percentage removal efficiency (>95-98%) among heavy metal analytes studied (Cd, Pb, and Zn; Sun & Davis, 2007). Another bioretention laboratory study using various types of soil media reported 90-99% Cd removal efficiencies (J. Wang et al., 2016). This same study found evidence of Cd filtration being the primary mechanism of Cd removal as the majority of accumulation occurred in the surface layer. Cd has a moderate affinity for suspended solids, and is mostly found in dissolved and colloidal state within urban stormwater runoff (Makepeace et al., 1995; Maniquiz-Redillas & Kim, 2016; Prestes et al., 2006). Soil in bioretention media has a high cation exchange capacity, and Cd species present in stormwater runoff have high binding and sorption affinities (Loganathan et al., 2012; Muthanna et al., 2007). This means Cd readily binds to clay, silt, and organic matter particles within GI (Naidu et al., 1997).

Table 12: Summary statistics for concentrations and loads of heavy metals by project phase at Cooke-Glenmont (CG) and Indian Springs (IS). Interpretations related to project phase were made using an ANCOVA. Comparisons to the control were done using a t-test on the post-GI data only.

	Pollutant	Site	Baseline or Pre-GI Phase			Post-GI Phase			Statistical Results			
			n	Control Median	Treatment Median	n	Control Median	Treatment Median	LSM % Difference	t-value	p-value	Interpretation
Concentration (µg/L)	Cd	CG	19	0.120	0.200	46	0.070	0.079	-64.3	0.61	0.548	NSD with control
		IS	20	0.105	0.115	17	0.066	0.041	-69.6	-	-	-
	Cr	CG	19	3.4	1.9	46	3.6	1.8	1.9	-6.76	2.330E-08	CG < Control
		IS	20	3.4	2.4	17	3.0	1.9	-24.7	-	-	-
	Cu	CG	19	11.3	15.4	46	8.3	9.7	-35.1	3.34	0.001	Baseline > Post-GI*
		IS	20	11.7	12.4	17	6.4	7.8	-37.0	0.73	0.478	NSD with control
	Ni	CG	19	2.65	7.70	46	2.40	5.05	-35.6	13.17	4.757E-17	CG > Control
		IS	20	2.45	4.20	17	2.60	2.70	-14.2	-	-	-
	Pb	CG	19	6.7	9.4	46	4.9	4.1	-48.7	1.60	0.114	NSD btw. phase*
		IS	20	5.8	4.7	17	4.1	2.3	-58.3	-	-	-
	Zn	CG	19	70.6	50.0	46	37.3	32.7	-25.2	1.36	0.180	NSD btw. phase*
		IS	20	68.3	54.8	17	30.4	24.8	-45.5	-	-	-
Load (g/ha)	Cd	CG	16	0.0061	0.0057	46	0.0023	0.0020	-68.9	-2.76	0.008	Baseline > Post-GI
		IS	17	0.0030	0.0044	15	0.0021	0.0018	-63.3	-	-	-
	Cr	CG	16	0.08	0.06	46	0.13	0.07	-5.1	-2.28	0.026	Baseline > Post-GI
		IS	17	0.06	0.10	15	0.07	0.13	-8.6	-	-	-
	Cu	CG	16	0.43	0.45	46	0.36	0.36	-37.5	-2.51	0.015	Baseline > Post-GI
		IS	17	0.37	0.50	15	0.23	0.51	-21.3	-	-	-
	Ni	CG	16	0.12	0.24	46	0.09	0.20	-40.0	-2.14	0.036	Baseline > Post-GI
		IS	17	0.07	0.19	15	0.06	0.16	2.1	-	-	-
	Pb	CG	16	0.23	0.28	46	0.21	0.17	-52.3	-2.04	0.046	Baseline > Post-GI
		IS	17	0.19	0.22	15	0.14	0.16	-50.5	-	-	-
	Zn	CG	16	2.34	1.31	46	1.43	1.24	-26.5	-3.26	0.002	Baseline > Post-GI
		IS	17	1.56	2.48	15	1.02	2.11	-32.46	-	-	-

Note: NSD implies no significant difference, while dash (-) indicates that statistical analyses were not performed due to insufficient sample size or data failing to meet model assumptions, * indicates a significant difference was observed in ANCOVA slopes, whereas the p-value indicates a significant difference in ANCOVA intercepts, negative LSM % differences imply reductions.

2.3.4.2 Chromium

Cooke-Glenmont had significantly lower concentrations of Cr than Beechwold during the post-GI phase (Table 12; $p<0.001$). Since this significant difference also existed during the pre-GI phase, perhaps differences in Cr concentrations were related to land use. Anthropogenic Cr is sourced from areas related to buildings and urbanization, and Beechwold had more imperviousness, greater commercial land use, and less woody vegetation than Cooke-Glenmont. Baseline and post-GI Cr concentrations for Cooke-Glenmont of 1.9 and 1.8 µg/L, respectively, and pre- and post-GI Cr concentrations at Indian Springs of 2.4 and 1.9 µg/L were all less than the median effluent Cr concentrations for bioretention (2.50 µg/L) and permeable pavement (4.28 µg/L) reported for single BMPs in the International Stormwater BMP Database (Clary & Jones, 2016). This implies low concentrations of Cr originally existed at Cooke-Glenmont and Indian Springs, so further reductions through GI practices were not likely. The BMP database showed bioretention significantly reduced Cr EMCs in stormwater runoff by 21.9%. A similar reduction occurred at Indian Springs, where the concentration of Cr showed a non-significant 24.7% decrease.

A significant 5.1% decrease in Cr loading was demonstrated at Cooke-Glenmont between baseline and post-GI phases ($p<0.05$; Table 12). Since no difference was observed in Cr concentration with project phase, but a significant difference was in loading, Cr load reduction at Cooke-Glenmont is likely due to the attenuation of runoff volume by GI. Since no significant difference was observed in Cr concentration with project phase, significant Cr load reduction at Cooke-Glenmont was likely due to the attenuation of runoff volume by GI. A field study of bioretention in Maryland demonstrated effective chromium load reductions through both runoff volume attenuation and concentration reductions (H. Li & Davis, 2009). The Cr loading reduction was only 5.1% at Cooke-Glenmont because only 30.1% of the sewershed was treated by GI, and a low concentration of Cr originally existed in the sewershed.

2.3.4.3 Copper

Cu EMC decreased by 35.1% and 37.0% at Cooke-Glenmont (Table 12; $p<0.001$) and Indian Springs (not significant), respectively, following GI installation. These were similar to the 38.0% and 35.8% reductions in median Cu concentrations reported by the International Stormwater BMP Database for runoff through single bioretention cells and permeable pavement, respectively (Clary & Jones, 2016). Cu was the only heavy metal analyte presented herein to demonstrate a significant EMC reduction with the installation of GI at Cooke-Glenmont. Cu in stormwater runoff is preferentially bound to particulate matter to a greater extent than Cd and Cr, demonstrating a moderate (48%) affinity for TSS (Birch & Rochford, 2010; Prestes et al., 2006). Dissolved Cu in stormwater has been shown to have the highest competitive sorption of the among the heavy metals discussed herein (Jalali & Moradi, 2013). Further evidence of Cu sorption at Cooke-Glenmont was provided since bioretention was better suited to treat smaller storm events than larger storm events (Figure 8). Smaller storms have longer hydraulic retention times, allowing for more sorption and sedimentation of Cu from runoff. Other residential GI studies also credited high Cu concentration reductions to both sorption and sedimentation in GI (Page et al., 2015; J. Wang et al., 2017). Meanwhile, other urban studies of two bioretention cells or a residential GI sewersheds less than 1 ha demonstrated 31-62% Cu EMC reductions with the installation of GI (H. Li & Davis, 2009; Page et al., 2015). These reductions were comparable to GI studies presented herein, meaning GI is capable of treating Cu EMCs at sewersheds less and greater than 10 ha. Given only 30.1% of Cooke-Glenmont was treated by GI, and that laboratory bioretention studies reported Cu EMC reductions in the range of 87-98% (Davis et al., 2001; Sun & Davis, 2007), excellent Cu removal occurred for the treated surface area.

Meanwhile the median Cu EMC at Indian Springs was not significantly different than Beechwold during the post-GI phase ($p>0.45$; Table 12). This is reasonable as both Cooke-Glenmont and Beechwold were residential areas, and automobiles and metal piping are Cu sources (Brown & Peake, 2006; McKenzie et al., 2009; Singh et al., 2011). Cu storm event loads decreased by 37.5% and 21.3%, respectively, at Cooke-Glenmont ($p<0.05$) and Indian Springs (not significant). Percent of the sewershed treated by GI appears to correspond with Cu storm load reductions. Whereas 30.1% of Cooke-Glenmont was treated by GI and a 37.5% Cu storm event load reduction was observed, 23.6% of Indian Springs was treated by GI and a 21.3% Cu storm event load reduction was observed. After future sampling, a significant Cu EMC and loading reduction is anticipated at Indian Springs due to the high competitive sorption behavior of dissolved Cu, sedimentation of particulate within Cu within GI, and runoff attenuation.

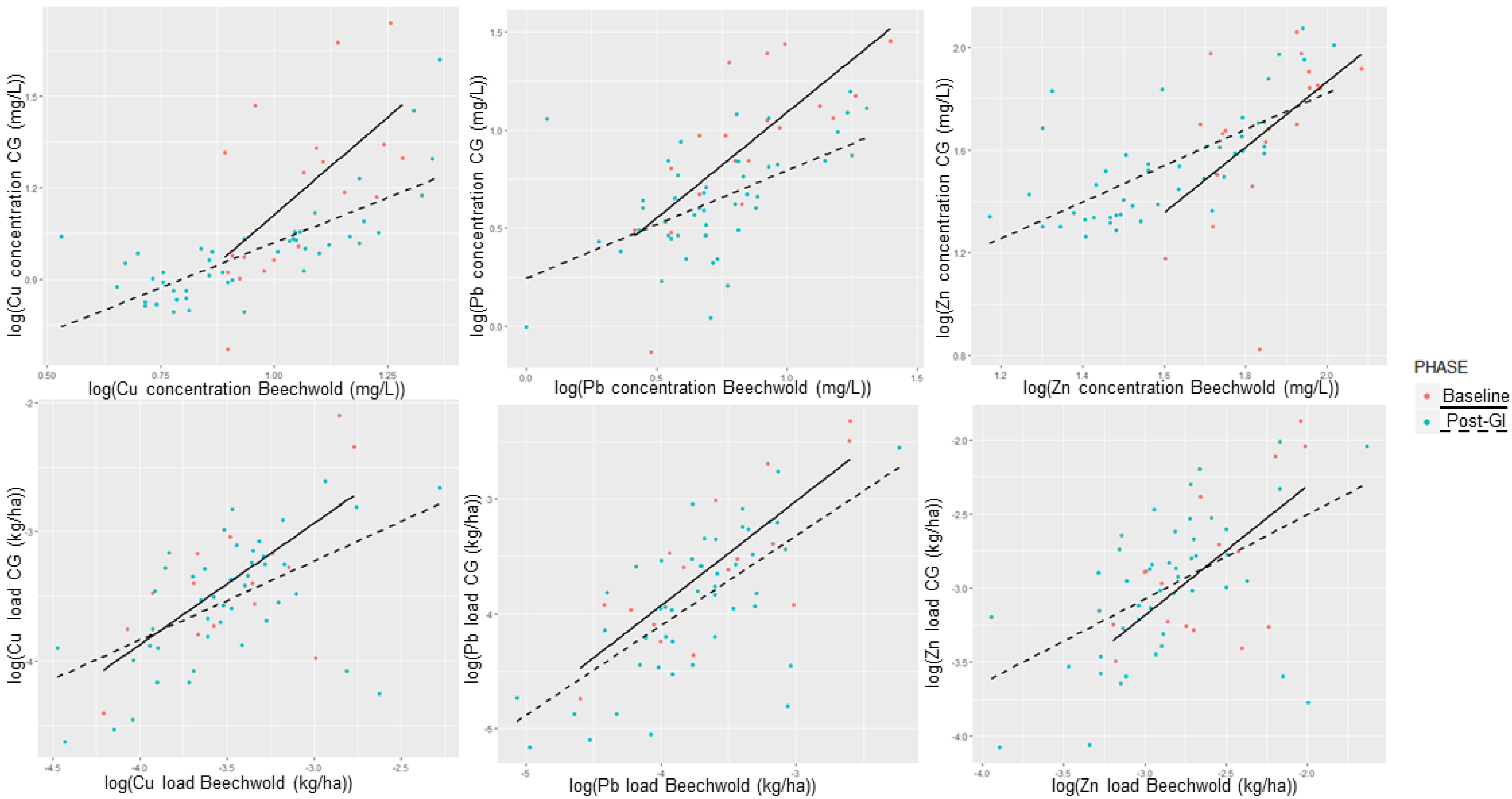

Figure 8: ANCOVA models for Cu, Pb, and Zn concentrations and storm event loads at Cooke-Glenmont. Significant differences in intercepts were observed for storm event load for all heavy metals (p<0.05), but only Cu concentration (*p*<0.001). Significant differences in slopes were observed for Cu and Pb concentrations (*p*<0.01).

2.3.4.4 Lead

Pb EMC insignificantly decreased by 48.7% and 58.3% at Cooke-Glenmont and Indian Springs with the installation of GI (Table 12). A significant difference was, however, observed in the slopes at Cooke-Glenmont ($p<0.01$), meaning GI is better suited to reduce Pb EMCs for smaller storm events (Figure 8). Substantial reductions in Pb storm event load were observed at Cooke-Glenmont (52.3%, $p<0.05$) and Indian Springs (50.5%, not significant). Substantial Pb concentration reductions were also reported by the International Stormwater BMP Database, where 89.9% and 83.0% reductions were observed as runoff passed through single cell bioretention and permeable pavement, respectively. Given only 30.1 and 23.6% of the sewershed area was treated by GI at Cooke-Glenmont and Indian Springs, respectively, and Pb EMCs reduced by roughly 50%, substantial Pb sedimentation must have occurred in GI. This substantial Pb sedimentation is feasible because Pb has been shown to be the highest proportion particulate bound of the heavy metals presented herein (95 and 97% particulate bound in roof and yard runoff, respectively; Birch & Rochford, 2010; Gromaire-Mertz et al., 1999). Other studies of residential GI demonstrated significant, 67-89% Pb EMC reductions with the installation of GI (Bedan & Clausen 2009; Page et al., 2015). Laboratory bioretention studies demonstrated 95-97% Pb EMC reductions (Hsieh & Davis, 2005; Sun & Davis, 2007). Past permeable pavement studies demonstrated 79-92% reductions in Pb EMCs (Braswell et al., 2018; Scholz & Grabowiecki, 2007). This implies high rates of Pb removal was consistent across various settings and GI practices. Moreover, since significant TSS sedimentation occurred at Cooke-Glenmont (Table 5), particulate Pb was removed along with TSS. The significant loading decrease at Cooke-Glenmont was likely due to both concentration and runoff volume reductions by GI.

2.3.4.5 Nickel

Insignificant Ni EMC reductions of 35.6 and 14.2% were observed at Cooke-Glenmont and Indian Springs, respectively. Storm event loads were significantly reduced at Cooke-Glenmont (40.0%, $p<0.05$; Table 12), but not at Indian Springs (inadequate data size). The International Stormwater BMP Database also reported non-significant difference in Ni concentrations with bioretention treatment through single bioretention practices, but a significant 52.4% reduction as runoff passed through permeable pavement (Clary & Jones, 2016). Further post-GI median Ni EMC reduction is possible at Indian Springs (2.70 µg/L) because it is larger than the median effluent EMC for permeable pavement reported by the International Stormwater BMP Database (1.76 µg/L). Perhaps no significant differences were observed for Ni EMCs because of Ni characteristics. While still related to TSS, past studies demonstrated Ni having the lowest proportion of particulates of the heavy metals presented herein (Birch & Rochford, 2010), so Ni sedimentation likely occurred to a lesser extent within GI. The significant Ni load reduction was likely due to the GI practices reducing runoff volumes.

Median Ni concentrations were significantly higher at Cooke-Glenmont (5.05 µg/L) than Beechwold (2.40 µg/L) during the post-GI phase ($p<0.001$; Table 12). This was likely due to land use because Ni occurs naturally in vegetated areas, and Cooke-Glenmont had the greatest amount of natural, vegetated land use (Iyaka, 2011). Ni is largely related to organic matter (Makepeace et al., 1995). GI may sustain Ni EMCs since GI introduces more organics to a sewershed.

2.3.4.6 Zinc

The installation of GI resulted in non-significant 25.2% and 45.5% reductions in Zn EMC at Cooke-Glenmont and Indian Springs, respectively (Table 12). GI at Cooke-Glenmont was equally suited to reduce Zn EMCs from small and large storm events (Figure 8). Zn storm event loading decreased by 26.5% at Cooke-Glenmont ($p<0.005$) and 32.5% at Indian Springs (insufficient data size). Compared to these results at the sewershed scale, single bioretention cells and permeable pavement resulted in 75.9 and 75.6% Zn EMC reductions (Clary & Jones, 2016). This disparity with single practices is likely due to the percent of the watershed treated. At Cooke-Glenmont and Indian Springs, respectively, only 30.1 and 23.1% of the sewershed was treated by GI. The other areas of the sewershed may act as a source of Zn, as it is sourced from galvanized roofs, gutters, plumbing, and automobile traffic (Brown & Peake, 2006; Müller et al., 2020; Singh et al., 2011). Other residential GI studies saw Zn EMC reductions (76-77%) if they treated a larger percentage of the watershed (up to 91%; Page et al., 2015; Bedan & Clausen 2009). Another plausible explanation for the lack of significant Zn EMC reduction is Zn characteristics. While Zn does adsorb to TSS, it is largely related to dissolved solids (Makepeace et al., 1995). Compared with Pb and Cu, Zn has the lowest competitive metal sorption (Gülbaz et al., 2015; Jalali & Moradi, 2013). A combination of sewershed and Zn characteristics contributed to the non-significance in Zn EMC.

2.3.5 Annual Loading

TSS annual load reductions of 83.8 and 95.3% were observed at Cooke-Glenmont and Indian Springs, respectively (Table 13). These reductions are larger than reported LSM reductions for storm event load reported in section 2.3.3 because annual load reductions were calculated as a simple arithmetic mean. A significant difference existed in 5-minute peak rainfall intensity, with baseline or pre-GI having a higher peak intensity than post-GI. This difference was not accounted for using the simple arithmetic mean, so annual loading percent reductions are likely exaggerated. Other residential and commercial GI studies reported similar annual TSS load reductions of 92-97% (Page et al., 2015, Line et al., 2012), but they treated a larger, upwards of 90%, area of the sewershed. Pre-GI annual TSS loads of 2114 and 5198 kg/ha/yr for Cooke-Glenmont and Indian Springs, respectively, exceeded the 1958 kg/ha/yr annual TSS load reported for a residential neighborhood reported by Line et al (2012). Post-GI annual loads of 343 and 242 kg/ha/yr for Cooke-Glenmont and Indian Springs, respectively were substantially less than the typical TSS annual load for a developed area.

Table 13: Annual sediment and heavy metal pollutant load (g/ha/year) for sewersheds by project phase.

Pollutant	Beechwold	Cooke-Glenmont			Indian Springs			Page et al (2015)			Bedan and Clausen (2009)		
	Control	Baseline	Post-GI	% Diff	Pre-GI	Post-GI	% Diff	SCM Calibration	SCM Treatment	% Diff	Pre-LID	Post-LID	% Diff
TSS*	525	2114	343	-83.8	5198	242	-95.3	157	12	-92	3	8	85
Cd	0.04	0.14	0.04	-71.1	0.30	0.03	-90.6	-	-	-	-	-	-
Cr	1.61	1.47	1.26	-14.5	4.75	1.57	-66.9	-	-	-	-	-	-
Cu	4.07	10.93	5.76	-47.3	19.75	5.80	-70.6	39	3	-77	6	4	-50
Ni	1.16	5.27	2.53	-51.9	6.79	2.39	-64.8	-	-	-	-	-	-
Pb	2.99	8.61	2.55	-70.4	19.35	1.94	-90.0	51	5	-90	3	0.5	-79
Zn	19.74	32.71	17.38	-46.9	95.38	30.34	-68.2	191	36	-81	65	10	-81

*Reported in kg/ha/yr

Cd and Pb annual load reductions at Cooke-Glenmont were 71.1 and 70.4%, respectively, and 90.6 and 90.0% at Indian Springs, respectively (Table 13). The magnitude of Cd and Pb annual load reductions were most similar to TSS. Since Cd and Pb are majority sediment-bound, it is logical they exhibited annual load removal patterns similar to TSS. Rainfall characteristics and GI likely both impacted Cd and Pb annual loading. Other residential GI studies reported similar annual Pb load reductions of 79-90% (Page et al., 2015; Bedan and Clausen, 2009; Table 8). Having more GI practices and permeable pavement increased Cd and Pb annual load reductions by 20%.

Cu annual load reductions of 47.3 and 70.6% at Cooke-Glenmont and Indian Springs, respectively, were similar to those reported by other residential GI studies (50-77%; Page et al., 2015; Bedan and Clausen, 2009; Table 13). Zn annual load reductions of 46.9 and 68.2% at Cooke-Glenmont and Indian Springs, respectively, were less than those reported by other residential GI studies (both 81%; Page et al., 2015; Bedan and Clausen, 2009). GI density and type likely do have an impact on Cu and Zn annual load reductions, as having a greater number of bioretention facilities and permeable pavement improves Cu and Zn annual load removal by roughly 20%.

Ni annual loading decreased by 51.9% at Cooke-Glenmont and 64.8% at Indian Springs (Table 13). Permeable pavement likely caused additional Ni removal beyond bioretention alone at Cooke-Glenmont. Cr annual loading reductions, on the other hand, varied upwards of 50% between the two sites (14.5% at Cooke-Glenmont and 66.9% at Indian Springs). This difference is related to the amount of Cr originally present in the sewershed. During the baseline phase at Cooke-Glenmont, the Cr annual load of 1.47

kg/ha/yr was less than the post-GI Cr annual load of 1.57 kg/ha/yr at Indian Springs. This implies a small amount of Cr originally existed at Cooke-Glenmont before the installation of GI, making further reductions with GI unlikely.

2.4 Summary and Conclusions

This study of residential sewersheds at a scale larger than 10 ha demonstrates metals and TSS removal benefits of GI. These benefits were realized at relatively low ratios of bioretention to sewershed area (0.38-1.91%). Bioretention and permeable pavement at treatment sewersheds significantly reduced TSS and heavy metal concentrations and loads. Conclusions drawn from this study include:

- Significant 61.6-67.7% TSS EMC reductions occurred at treatment sites, where similar reduction occurred regardless of varying GI density. GI was better suited to treat TSS during smaller precipitation events. Having fewer GI practices, while treating a larger percentage of the sewershed resulted in greater TSS load reduction.
- Bioretention at Cooke-Glenmont was better suited to treat Cu and Pb EMCs during small storm events. Zn EMC reductions at Cooke-Glenmont exhibited no significant difference regardless of small or large storm events.
- Cu was the only heavy metal discussed herein to demonstrate a significant reduction in EMC with the installation of GI. This likely occurred because compared to other heavy metals in stormwater, Cu is largely associated with dissolved solids and has a high competitive sorption. Further Cu reduction likely

occurred with the filtering and sedimentation of particulates within GI. Similar Cu EMC reductions (35.1 and 37.0%) occurred regardless of GI density. Having fewer GI practices while treating a larger percentage of the sewershed resulted in greater Cu load reductions.

- Significant reductions in loading were observed for Cd, Cr, Cu, Ni, Pb, and Zn following retrofit with GI. Since a significant EMC reduction with the installation of GI was only observed in the case of Cu, significant load reductions were likely due to runoff reduction provided by GI.
- Generally, percent EMC reductions with the installation of GI followed the trend Cd>Pb>Cu>Zn>Ni>Cr. Percent load reduction followed the trend Cd>Pb>Cu>Zn>Cr>Ni. Analytes demonstrating a high particulate percentage or large competitive sorption exhibited greater percent EMC reductions.

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